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Institut für Energie- und Klimaforschung
Nukleare Entsorgung und Reaktorsicherheit (IEK-6)

8th European Summer School on Separation Chemistry and Conditioning as well as Supramolecular, Intermolecular, Interaggregate Interactions

Stefan Neumeier, Philip Kegler und Dirk Bosbach (Hrsg.)

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JÜLICH
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Summer School Program

8th European Summer School

on

Separation Chemistry and Conditioning

as well as

Supramolecular, Intermolecular, Interaggregate Interactions

Stefan Neumeier, Philip Kegler, Dirk Bosbach

July, 07 – 09, 2014 | Gustav-Stresemann-Institut | Bonn/Bad Godesberg, Germany

Organized by:

Contents

Summary

The Summer School will call leading scientist from France, Russia and Germany in the fields of solid state chemistry, supramolecular chemistry, colloid systems stability, formation, structure and interparticle interactions, with a particular emphasis on the applications to separation chemistry. Special attention will be given to these topics in relevance to nuclear waste management, lanthanide/actinide separation and transport of actinides in the environment. The participants will address directly the critical gaps in the understanding of processes crucial for safe nuclear waste disposal, decontamination/remediation technologies, separations in nuclear waste cycle etc.

A special objective of the Summer School will be the promotion of international collaborations and strengthening of discussions in order to identify and to fill the conceptual gaps in knowledge that are relevant for the nuclear fuel cycle and particular for the safe disposal of nuclear waste in a deep geological repository.

The Summer School will cover important topics that are related to international research efforts, several projects (BMBF, EC FP-7) and various bilateral collaborations. The School aims at stimulating effective scientific discussions on the institutional level and enhancing joint applications to unique pooled facilities like synchrotrons, actinide laboratories, etc.

Special attention will be paid to young researches in these fields to support their research mobility to other institutes.

Organisation:

Dr. Stefan Neumeier / Dr. Philip Kegler / Prof. Dr. Dirk Bosbach
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Agenda

Monday, 07th July 2014

12.00h Registration & welcome coffee

13:00h Welcome address (S. Neumeier, D. Bosbach)

13:30h *Dirk Bosbach:* Radionuclide solubility control in solid solution – aqueous solution systems: Radium solubility in the presence of barite

14:15h Coffee Break

1st Session: „Partitioning“

14:45h *Andreas Wilden:* Development & demonstration of Actinide separation processes in Europe

15:20h *Julien Cambedouzou*: Measuring the specific surface area of powdered mesoporous solids using x-ray scattering

15:55h *Sandrine Dourdain:* Reverse aggregates of extractant as chemical separation system

16:30h Coffee Break

17:00h *Stéphane Pellet-Rostaing*: Multi-functional molecules used in complex formulations of extracting fluids

17:35h *Michel Meyer*: Uptake of f-elements by iron chelators: what can we learn from thermodynamic and kinetic solution studies?

19:30h Dinner (Restaurant @ Gustav-Stresemann Institut)

Agenda

Tuesday, 08th July 2014

2nd Session „Conditioning“

09.00h *Stefan Neumeier:* Immobilization of long-lived radionuclides after incorporation into repository relevant ceramics (Conditioning)

09:35h *Nicolas Dacheux*: Monazite as a suitable long-term radwaste matrix? Insights coming from chemistry and geochemistry

10:10h Coffee Break

10:40h *Nicolas Clavier:* New challenges in the sintering of nuclear ceramics

11:15h *Igor Alencar :* Radiation effects in solids

12:15h Lunch

3rd Session „Advanced methods in nuclear science“

14:00h *Henry Moll*: Microorganisms and their impact on radionuclide speciation

14.35h *Evgeny Alekseev:* Solid state actinide chemistry and structural research in Jülich

15.10h Coffee Break (Poster Mounting)

15:45h *Yan Li*: Nuclear waste management on supercomputers: Reliable modelling of f-elements-bearing ceramic materials

16:10h *Thomas Zemb:* Origins of solvent phase instabilities in multi-phase liquid-liquid extraction

18:00h Dinner (Fingerfood) & Poster Session

Agenda

Wednesday, 09th July 2014

4th Session „Radionuclide Mobility& Migration“

08:30h *Felix Brandt:* Dissolution kinetics of nuclear waste forms - an introduction

09:05h *Katja Schmeide*: Uranium(VI) retention in clay and crystalline rock: How and why does it differ?

09:45h Coffee Break

10:30h *Thorsten Schäfer:* Colloid/Nanoparticle formation and radionuclide mobility determining processes investigated by laser- and synchrotron based techniques

11:05h *Stefan Neumeier:* Summary and end of the meeting

12:15h Lunch

After lunch: Departure

Lectures		
Surname	**Name**	**Affiliation**
Alekseev	Evgeny	Solid state actinide chemistry and structural research in Jülich
Alencar Vellame	Igor	Radiation effects in solids
Bosbach	Dirk	Radionuclide solubility control in solid solution –aqueous solution systems: Radium solubility in the presence of barite
Brandt	Felix	Dissolution kinetics of nuclear waste forms - an introduction
Cambedouzou	Julien	Measuring the specific surface area of powdered mesoporous solids using x-ray scattering
Clavier	Nicolas	New challenges in the sintering of nuclear ceramics
Dacheux	Nicolas	Monazite as a suitable long-term radwaste matrix ? Insights coming from chemistry and geochemistry
Dourdain	Sandrine	Reverse aggregates of extractant as chemical separation system
Li	Yan	Nuclear waste management on supercomputers: Reliable modelling of f-elements-bearing ceramic materials
Meyer	Michel	Uptake of f-elements by iron chelators: what can we learn from thermodynamic and kinetic solution studies?
Moll	Henry	Microorganisms and their impact on radionuclide speciation
Neumeier	Stefan	Immobilization of long-lived radionuclides after incorporation into repository relevant ceramics (Conditioning)
Pellet-Rostaing	Stéphane	Multi-functional molecules used in complex formulations of extracting fluids
Reich	Tobias	Speciation of actinides using synchrotron radiation techniques
Schäfer	Thorsten	Colloid/Nanoparticle formation and radionuclide mobility determining processes investigated by laser- and synchrotron based techniques
Schmeide	Katja	Uranium(VI) retention in clay and crystalline rock: How and why does it differ?
Wilden	Andreas	Development & demonstration of actinide separation processes in Europe
Zemb	Thomas	Origins of solvent phase instabilities in multi-phase liquid-liquid extraction

Poster session

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Bauer	Johannes	Materials properties at high pressure in the diamond anvil cell
Beridze	George	Atomistic modelling for nuclear waste management
Bukaemskiy	Andrey	Stability of pyrochlore phase for zirconia based ceramics. Experimental and modeling study
Darbha	Gopala	Quantification of interaction forces between clay colloid edge sites and mineral surfaces
Ebert	Elena	Electrospray ionization time-of-flight mass spectrometry: Dissolution of Mo-based CERMET fuel
El Ouzzani	Hasnaa	Interfacial dynamic in liquid/liquid extraction processes probed by non-linear optics
Finkeldei	Sarah	*s. abstract Felix Brandt*; Dissolution kinetics of nuclear waste forms - an introduction
Fritsch	Katharina	Influence of ionic strength on U(VI) sorption on montmorillonite at high salinities
Gausse	Clémence	Solubility properties of the Ln-rhabdophane compounds: $LnPO_4.nH_2O$ (Ln = La → Dy), precursor of the monazite phase
Heuser	Julia	Experimental and computational simulation of radiation damages
Hirsch	Antje	Optical floating zone method and accelerated crucible rotation technique - Two different approaches of growing single-crystals -
Kegler	Philip	Actinide chemistry under extreme conditions: the new high pressure / high temperature facility at Jülich research center
Klepov	Vladislav	Single crystal X-ray diffraction and its application in actinide studies
Lopian	Tobias	Extraction of Ta and Nb with an alternative procedure using the pre-ouzo effect
Lozano-Rodriguez	Janeth	X-ray absorption fine spectroscopy on the Rossendorf Beamline
Matveev	Petr	Comparison of mass-spectrometry, atomic emission spectrometry and gamma spectrometry for determination of rare earth elements.
Mesbah	Adel	The monoclinic form of the rhabdophane compounds: $REEPO_4 \cdot 0.625.H_2O$
Middendorp	Ronald	Preparation of microparticle reference materials for nuclear safeguards particle analysis
Obruchnikova	Yana	Solubility thermodynamics of tetrapropyl- and tetrabutylammonium pertechnetates
Omanovic	Sanela	Non-nuclear applications - Separation of rare earth elements
Rey	Julien	Synergistic mechanism in liquid-liquid extraction: role of water - effect on interfacial film curvature
Rosemann	Jonathan	Micro-scale study of Np speciation during diffusion in natural clay
Schmidt	Holger	Radiation stability of partitioning relevant ligands for minor actinide separation
Scholze	Raphael	Sorption of Pu(III) onto Opalinus Clay – Influence of pH and ionic strength
Schönberg	Pascal	Ultratrace analysis of Pu, Np and Tc using Resonance Ionization Mass Spectrometry (RIMS)
Schreinemachers	Christian	Production of simulated fuel particles and analytical characterization methods
Semenkova	Anna	Determination of La and Eu by ICP-AES and gamma-spectrometry
Senik	Nadezhda	Application of gamma-spectrometry and LSC and for determination of rare earth elements
Solovov	Roman	Preparation of palladium nanoparticles by photolysis and evolution of physicochemical properties
Thust	Anja	Plane wave parallel plate ultrasound spectroscopy on ceramic pellets
Torapava	Natallia	Immobilization of long-lived iodine after incorporation into apatite and layered double hydroxide matrices
Volostnykh	Marina	Metal(III) complexes of meso-phosphorylated porphyrins: synthesis and self-assembling
Weber	Juliane	Combined chemical and structural investigations of $Ba_xRa_{1-x}SO_4$ on the atomic level by TEM and APT
Willberger	Christian	Redox speciation of neptunium using capillary electrophoresis coupled to ICP-MS
Yu	Na	*s. abstract Vladislav Klepov*; Single crystal x-ray diffraction and its application in actinide studies
Zappey	Joaquina	Knudsen effusion mass spectrometry

Abstracts

Solid state actinide chemistry and structural research in Jülich

Evgeny V. Alekseev[1,2]

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Main results in the field of actinide solid state chemistry and structural studies obtained in IEK-6, Forschungszentrum Jülich will be presented within the talk. Current researches are almost focused on investigation of early actinides behavior in oxo-salts systems. It includes a study of formation, structures, stability and properties of actinide borates, silicates, phosphates/arsenates, selenates, molybdates and tungstates. Several methods were used to study the structures of obtained compounds: X-ray diffraction including both single crystal and powder methods; Raman, IR and UV-vis-NIR spectroscopy; high temperature XRD; micro-XANES; solid state NMR. The complex of these methods allows performing a detailed study of atomic structures of actinide phases including determination of valence states of actinides centers and structures of disordered fragments.

Radiation effects in solids

Igor Alencar

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In this talk, I will present a general overview of radiation effects in solids and their consequences regarding the choice of suitable matrices for the immobilization of nuclear waste. I will discuss the mechanisms of primary energy transfer from an energetic particle incident onto a solid and the still open question of how to characterize the effect of a particle beam (e.g. linear energy transfer, displacements per atoms, etc.). Results from irradiation experiments, employing techniques such as selected area electron diffraction and Rutherford backscattering spectrometry, will be used to illustrate the concepts. Another aspect which will be introduced is the critical amorphization temperature, which seems to play a key role when irradiation experiments have to be compared with natural analogues. Finally, conclusions concerning the radiation-resistance suitability of potential matrices will be given.

Time-resolved laser-fluorescence spectroscopy (TRLFS) – A spectroscopic tool to investigate f-element interactions in solids and solutions on the molecular level

N. Huittinen[1], Yulia Arinicheva[2], J. Holthausen[2], S. Neumeier[2], N. Baumann[1], T. Stumpf[1]

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Time-resolved laser-fluorescence spectroscopy (TRLFS) is a spectroscopic technique with outstanding sensitivity, based on the spontaneous emission of light. Spontaneous emission of light or luminescence describes the process of radiative decay where an excited substance emits electromagnetic radiation upon relaxation. Some f-elements, such as the actinides U^{4+}, and Cm^{3+}, and the lanthanide Eu^{3+}, relax through intense luminescence emission from an excited f-state to the ground f-level. These f-f transitions are sensitive to changes in the ligand field, thus, making TRLFS an extremely useful tool to account for the complex speciation of these elements. Depending on the f-element, the recorded emission spectra can provide information on e.g. the complexation mechanism of the ion on a solid surface or the symmetry of the adsorption/incorporation site of the metal. Information about the hydration state of the f-element cation can be gained from the fluorescence lifetime, i.e. the residence time in the excited state. In aquatic environments f-element spectroscopy is characterized by relatively short fluorescence lifetimes due to the transfer of electronic energy from an excited f-level to the vibrational levels of water molecules in the first coordination sphere of the metal. When some of these quenching entities are lost upon inner sphere surface complexation a longer lifetime is acquired, thus, providing information on the sorption mechanism. If incorporation occurs, the complete hydration sphere is replaced by the ligands of the crystal lattice and the lifetimes become very long.

In the present work we have used site-selective TRLFS to investigate the structural incorporation of Eu^{3+}, as an analogue for Pu^{3+}, Am^{3+} and Cm^{3+} found in spent nuclear fuel, in rare earth phosphate ceramics. These crystalline ceramic materials show promise as potential waste forms for immobilization of high-level radioactive wastes due to their stability over geological time scales [1] and their tolerance to high radiation doses [2]. The $REPO_4$ crystallize in two distinct structures, depending on the ionic radius of the cation: the larger lanthanides (La^{3+} to Gd^{3+}) crystallize in the nine-fold coordinated monazite structure, the smaller ones as Lu^{3+} form eight-fold coordinated xenotime structures. Here, we present results on the influence of the ionic radius of the host cation and the crystalline structure of the $REPO_4$ on Eu^{3+} substitution in the ceramic.

[1] Donald *et al.* (1997) *J. Mater. Sci.* **32**, 5851-5887.
[2] Luo & Liu (2001) *J. Mater. Res.* **16**, 366-372.

Materials properties at high pressure in the diamond anvil cell

Johannes D. Bauer[1], S. Labs[2], L. Bayarjargal[1] and B. Winkler[1]

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The diamond anvil cell (DAC) is a widely used tool to generate high pressures of up to a few megabars. The sample is contained in a hole (diameter ~ 100 µm) in a gasket (thickness ~ 50 µm) that is squeezed between the two diamonds (see figure 1). High temperatures up to 1200 K can reached by resistive heating, sample temperatures up to a few thousand K can be achieved by laser heating [1].

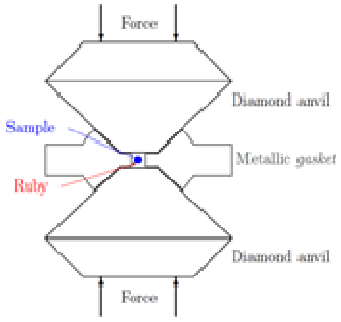

Figure 1: Schematic of a DAC

As diamond is transparent for a wide part of the electromagnetic spectrum including visible light, samples can be investigated by various spectroscopic techniques and X-ray diffraction. The pressure is routinely determined by the measurement of the pressure dependent fluorescence shift of a ruby fluorescence line [2]. Raman spectroscopy can be employed to measure vibrational spectra of materials at high pressure in the DAC and investigate e.g. pressure induced structural phase transformations.

Figure 2 depicts the pressure dependence of the Raman modes (left) and the unit cell volume (right) of $USiO_4$ from experiments and DFT+U calculations. The synchrotron powder diffraction experiments show a reversible phase transformation of the low pressure phase with zircon structure (coffinite) to a high pressure phase with scheelite structure. The Raman spectra of the high pressure form could not be measured [3].

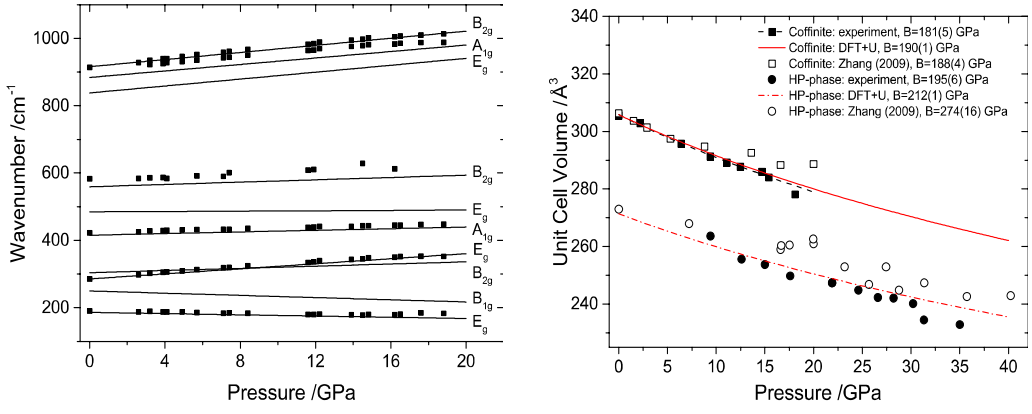

Figure 2 left: Pressure dependence of the Raman modes of $USiO_4$. The experimental values are depicted by squares, the lines represent the mode positions from DFT+U calculations. Right: Unit cell volumes of the low and high pressure phases of $USiO_4$ as a function of pressure.

[1] N. Dubrovinskaia and L. Dubrovinsky: *Rev. Sci. Instrum.* 74 (2003), 3433–3437; W.A. Bassett: *Rev. Sci. Instrum.* 72 (2001), 1270–1272

[2] H.K. Mao et al.: *J. Geophys. Res. B: Solid Earth* 91 (1986), 4673–4676

[3] J.D. Bauer et al.: submitted for publication

Atomistic modelling for nuclear waste management

George Beridze, Y. Li & P. Kowalski

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In the IEK-6, the Nuclear Waste Management part of the Institute of Energy and Climate Research at Forschungszentrum Jülich we are establishing a virtual laboratory that allows us for atomic-scale modelling of the materials relevant for the nuclear waste management. In this contribution we will show what kind of research studies could be performed using the leading supercomputing resources and the state-of-the-art computational software and how it can complement the ongoing experimental work. We will present some of our results that illustrate modelling of various structural, thermodynamical and mechanical properties of radionuclide-bearing materials. We will also show how the various spectral signatures (including X-rays, IR and Raman spectroscopies) could be computed and how such a result could help in the interpretation of the measured spectral signatures of the new materials.

Radionuclide solubility control in solid solution –aqueous solution systems: Radium solubility in the presence of barite

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The migration of radionuclides in the geosphere is to a large extend controlled by sorption processes onto minerals and colloids. On a molecular level, sorption phenomena involve surface complexation, ion exchange as well as co/precipitation reactions. Coprecipitation leads to the formation of structurally incorporated radionuclides in a host structure. Such solid solutions are ubiquitous in natural systems – most minerals in nature are atomistic mixtures of elements rather than pure compounds. In many cases the formation of solid solutions leads to a thermodynamically more stable situation compared to the formation of pure compounds, due to a negative excess Gibbs energy of mixing. Deriving a thermodynamic model requires a molecular level concept including information such as the actual substitution mechanism, site occupancies and related ordering phenomena.
However, radionuclide solubility controlled by solid solutions is currently not considered in long term safety assessments for a nuclear waste repository system. One reason is related to the fact that only a limited number of rather simple solid solution systems have been studied to a sufficient level. Nevertheless, the thermodynamic concepts for solid solution formation under repository relevant conditions are very well developed. The importance of a molecular level mixing model should be emphasized. Furthermore, analytical tools (as well as computational approaches) to identify involved species, to characterize the mixing behavior at molecular scales and to derive thermodynamic data are available (even to work on complex solid solutions).
The control of Radium solubility in $(Ra,Ba,Sr)SO_4$ solid solution – aqueous solution systems under relevant conditions will be discussed. In general, its solubility is significantly reduced if it is controlled by a binary $(Ra,Ba)SO_4$ solid solution or an even more complex ternary $(Ra,Ba,Sr)SO_4$ solid solution. New experimental data obtained within the european project SKIN as well as computational approaches using first principle calculations will be discussed. In particular with respect to the conditions of interest here, one quest always needs to be considered: Do measured data of the solid solution and the aqueous solution represent equilibrium conditions or do they represent a metastable situation? The challenge to derive thermodynamic data from experiments in aqueous solution at rel. low temperatures with potentially metastable states will be discussed.

Dissolution kinetics of nuclear waste forms - an introduction

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Dissolution and recrystallization processes are a global phenomenon which occurs as soon as water and solids which are not in equilibrium come into contact. Geological processes such as transport and deposition, weathering and erosion, mineral dissolution and precipitation are often times kinetically controlled and therefore path dependent.

In scenarios for the safe management of nuclear waste, the waste form itself is often considered as an engineered barrier. Therefore it may significantly contribute to the overall performance of a particular deep geological waste repository. In this case the processes of dissolution, re-precipitation and the solubility of a particular waste form become relevant for the performance assessment. Here we will focus on theoretical and experimental aspects of the dissolution kinetics of nuclear waste forms.

Depending on the type of waste form and the predominant conditions dissolution and/or formation of secondary phases may occur. The most commonly cited dissolution rates are obtained in macroscopic experiments which are either designed to determine far-from equilibrium dissolution rates or to precipitate and later analyze secondary phases. Different types of macroscopic experiments will be discussed in the poster and oral presentation given by the authors.

The main idea of the macroscopic approach was to derive a predictive model for the dissolution of solids based on the separation of variables such as temperature and ionic strength. A classic example is the Lasaga rate equation [1]. Within this approach the particular influence of the independent variables on the dissolution rate can be derived :

$$Rate = k_0 \cdot A_{reactive} \cdot e^{-E_a/RT} \cdot a_{H^+}^{n_{H^+}} \cdot \Pi a_i^{n_i} \cdot f\left(\Delta G_r\right)$$

During the oral presentation the different aspects of this rate equation and its origin in the transition state theory (TST) and the surface complexation models of Stumm et al. [2] will be discussed. Recently, the reactive surface area or the surface reactivity has been identified as a key parameter for a truly mechanistic understanding of the dissolution kinetics. Based on an example the possible extension of macroscopic dissolution experiments by microscopic approaches will be shown and the strength and weakness of different attempts to describe the dissolution of nuclear waste forms will be presented.

[1] Lasaga A. (1995) Fundamental approaches in describing mineral dissolution and precipitation rates. *Rev. Mineral. Geochemistry*, 31, 23-86

[2] Stumm W. and Morgan J. J. (1996) Chemical equilibria and rates in natural waters. *Aquatic Chemistry*

Stability of pyrochlore phase for zirconia based ceramics. Experimental and modeling study

Andrey A. Bukaemskiy, S. Finkeldei, F. Brandt, S. Neumeier, G. Modolo, D. Bosbach

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The materials with the pyrochlore crystal structure are characterized by high physicochemical and important technological properties including catalytic activity, high ionic conductivity, luminescence, giant magnetoresistance and etc. Moreover, zirconia based pyrochlore ceramics are very promising candidates as potential waste forms for the conditioning of minor actinides (MA = Cm, Am, Np), because they are very stable against corrosion, radiation damages and also chemically very flexible. Therefore, the existence region of pyrochlore and its phase stability are key questions for the theoretical (modeling) studies and for technological applications.

In the present work, ZrO_2-Nd_2O_3 powders were studied by XRD with a detailed analysis of Bragg reflection shapes. The Hall-Williamson method was used for the estimation of the crystallite size and lattice distortions. Here neodymium serves as surrogate for the trivalent actinides.

The obtained results allow us to define the phase boundaries for the pyrochlore and defect fluorite crystal modifications more precisely. The changes of the lattice parameter (Vegard`s law), lattice distortion, crystallite size and microstructure features were studied in detail for a wide neodymia content region.

A criterion of stability of the pyrochlore phase was suggested and a direct correlation of this parameter and the lattice distortions was identified. In order to provide a complete overview of the stability fields of zirconia pyrochlore type ceramics, our new data are discussed together with available literature data on all types of pyrochlores. The new method of the delimitation of the pyrochlore stability field is proposed and discussed based on our experimental results and references taking into account the approximation of cation antisite disordering.

Measuring the specific surface area of powdered mesoporous solids using x-ray scattering

Julien Cambedouzou, and O. Dia

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The specific surface area of porous solids is usually measured using gas adsorption techniques. However, the latter methods are subjected to caution as the specific surface determination relies on debated estimations (surface covered by gas molecules…). Moreover, only the open porosity can be accessed by such measurements.
In this communication, we give an overview of the way small angle x-ray scattering (SAXS) can be used in order to quantify the specific surface area in porous granular materials. In particular, we present methodologies allowing experimentalists to adapt the formalism of the Porod limit to the case of granular solids. Examples from the literature will be presented [1], showing how the volume density of interface can be deduced from SAXS results on samples presenting two scales of sharp interfaces. We give a peculiar attention to the case of mesoporous silica possessing hexagonal lattices of cylindrical pores [2]. The SAXS profile of such samples does not show the typical Porod regime allowing the theorem of Porod limit to be used (see figure). Thanks to a numerical calculation of the SAXS profile of such sample, we show how it is possible to derive the specific surface originating from the surface of the mesopores. After comparison with the specific surface derived from gas adsorption measurements, we discuss the validity and limits of the SAXS-based method.

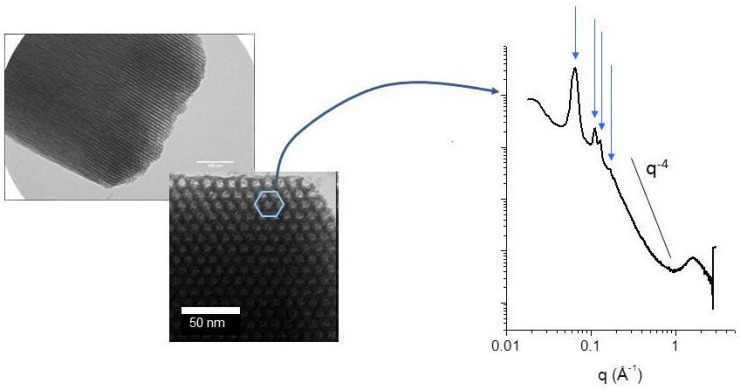

Figure: TEM and SAXS from a SBA-15 mesoporous silica.

[1] O. Spalla, S. Lyonnard, F. Testard, *J. Appl. Cryst.* 36, 338-347 (2003).
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New challenges in the sintering of nuclear ceramics

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Sintering is a key step in the elaboration of ceramic materials, which allows the transformation of powdered agglomerates into dense materials by the means of a heat treatment at high temperature. These processes are thus crucial in the nuclear fuel cycle, either during the elaboration of UOx or MOx fuels or in the framework of the development of ceramic matrices dedicated to the specific conditioning of several radionuclides. For both types of compounds, numerous works were then undertaken to precise the operating conditions (heating temperature, holding time, sintering atmosphere, …) leading to an optimal densification of the samples. Also, more and more studies aim to investigate more finely the mechanisms occurring during the densification step, mainly in order to provide an enhanced control of the final microstructure. This latter, which embraces the average grain size, the nature of the porosity, or the distribution of grain boundaries, is indeed frequently related to several properties in use such as the resistance to aqueous alteration or to radiation damages.

In this context, this talk will present in a first part the basics of sintering processes, with a short description of the various diffusion mechanisms involved and their respective influence on the final microstructure. Then, the methodology generally adopted to assess the behavior of ceramic nuclear materials, and particularly waste matrices, during densification will be described. In this aim, several examples coming from the study of monazite or Thorium-Phosphate-Diphosphate will be presented.

In a final part, a particular attention will be paid to the new experimental techniques developed to investigate *in situ* the sintering phenomena, including high temperature environmental scanning electron microscopy. Original results concerning, on the one hand, the behavior of spherical grains during the elaboration of necks, and, on the other hand, the grain growth kinetics at the surface of bulk materials will be emphasized. Also, new tools that allow an easier control of the microstructure will be proposed.

Monazite as a suitable long-term radwaste matrix? Insights coming from chemistry and geochemistry.

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In the last decades, several ceramic materials have been envisaged as potential matrices for long-term radwaste immobilization. Among them, monazite (LnPO4) appears as one of the most promising candidates owing to several physico-chemical properties including high structural flexibility and high chemical durability.

The original nine-fold coordination of the cation in the structure allows the formation of solid solutions through substitution mechanisms either on cationic or phosphate site. A large literature relates the formation of monazite phases incorporating various di-, tri or tetravalent elements as well as several polyoxoanions such as vanadates, silicates or even chromates. The simultaneous incorporation of tri- and tetravalent actinides can be performed in cheralite-type phases with the general formula : AnIII1-xMIIx-yMIVyPO4.

Furthermore, the monazite phase was usually reported to present several properties of interest in the field of the specific conditioning of radioactive elements, including transuranium elements (Np, Pu, Am, Cm). First, normalized dissolution rates obtained during leaching tests are always slow compared to that reported for other materials showing the high chemical durability of such ceramics. Moreover, the rapid precipitation of neoformed phases at the solid/liquid interface decreases significantly the release of elements through the apparition of diffusion phenomena.

The study of geological samples of monazites, naturally containing large amounts of thorium and / or uranium also allowed to evidence not only this very high chemical durability but also their good resistance to radiation damages. This talk will give an overview on the studies dedicated to this potential radwaste matrix, mainly concerning its high loading capability associated to its good resistance to dissolution.

Quantification of interaction forces between clay colloid edge sites and mineral surfaces

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Bentonite is often the recommended back-fill material in the context of safe disposal of radioactive waste in the geological repositories. Overtime, when ground water is in contact with bentonite, it may result in the formation of colloids and thus colloid-associated radionuclides may be transported along the micron scaled fractures that are naturally present in the underground repositories posing a potential threat to contaminate the nearby aquifers. Hence it is important to understand the interaction of bentonite clay colloids with granite (host rock: major constituents are biotite, quartz, plagioclase, K-feldspar) surfaces in the presence of radionuclides. Structurally, bentonite (the major component is montmorillonite) is made of two basic building blocks: the aluminium octahedral sheet and the silica tetrahedral sheet. Probing aluminol and silanol groups at clay edge sites determining the reactivity and metal ion interaction are a special focus of research.

Colloidal probes modified with Al_2O_3 and SiO_2 particles at the end of the AFM cantilever are used to mimic clay edge sites and estimate forces against mineral surfaces under varying pH and trace metal concentration, here Eu(III). With increasing pH (>6), as expected, a decrease in interaction forces between Al_2O_3 and SiO_2 particles with mineral surfaces (plagioclase, K-feldspar, quartz, biotite) was observed. Though Al_2O_3 and SiO_2 particles have similar adhesion forces towards mineral surfaces, at pH<6, SiO_2-K-feldspar and Al_2O_3-biotite are found to be higher compared to other colloid-mineral interactions. At pH 5, except for quartz, an increase in the [Eu(III)] from 0 to 10^{-5} M resulted in increase of adhesion forces between SiO_2 and mineral surfaces. In case of Al_2O_3, an increase in [Eu(III)] showed no significant change in interaction forces. At [Eu(III)]=10^{-5} M, the ratio $F_{adh(SiO2)}/F_{adh(Al2O3)}$ decrease in the order: 11.3 for biotite > 4.55 for plagioclase > 3.03 for K-feldspar > 0.22 for quartz. Interestingly, a change in the magnitude of adhesion forces (1.2 to 2 time) for four different alumina colloidal probes of similar size (8 µm) vs. a smooth biotite (Rq<1.2 nm) was observed, which is attributed to the rough features (of ~10 nm range) along colloidal particle verified by SEM and AFM, which demonstrates the influence of roughness on particle adhesion forces.

Reverse aggregates of extractant as chemical separation system

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Solvent extraction involves extractant molecules able to chelate selectively cations from a concentrated solution of mixed salts. Being amphiphilic, these molecules are also known to form reverse microemulsion in the organic phase, able to solubilize water and solutes. This double ability is at the origin of the molecular and supra molecular approaches that can be used to derive the mechanisms of solvent extraction. In this lecture, we'll focus on the less commonly studied supramolecular approach. Comparing extractant properties to surfactant's ones, we apply the thermodynamic equations of surfactant molecules, to estimate the importance of aggregation in solvent extraction mechanisms.

Electrospray ionization time-of-flight mass spectrometry: Dissolution of Mo-based CERMET fuel

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The electrospray ionization (ESI) method was developed by Dole and coworkers[1] to investigate macromolecules and coupled to a mass spectrometer for the first time in 1984 by Fenn et al.[2]. The method is primarily used for biomedical applications and the detection of large organic molecules. However, it is also extensively used in studies on metal ions in aqueous solution that are mainly aimed at determining elemental speciation, the interaction of metals with organic, and on the interaction of the metal ion with water or on hydrolysis. ESI is a very gentle ionization method, making fragmentation reactions unlikely. The spectra reflect the distribution of charged molecules in the solution. With this method also minor species can be detected. However, only charged species can be detected. Time-of-flight analysis of the ions covers a wide mass range at the same time and provides isobaric resolution.

The accelerator-driven systems (ADS) inert matrix fuel (IMF)[3-5] is a promising candidate for minor actinide (MA = Np, Am, and Cm) transmutation. The reprocessability of (Pu,MA)-oxide within a metallic ^{92}Mo matrix (CERMET) is under investigation within the EU project ASGARD[6]. Dissolution in nitric acid is the first step in reprocessing. Therefore, detailed knowledge of the speciation of molybdenum in nitric acid medium is crucial on the one hand to understand this dissolution process and on the other hand as a basis for the design of a tailored extraction process. Electrospray ionization mass spectrometry, which can probe the stoichiometry and relative abundances of solution species, was applied to extensively characterize and quantify the solution species of molybdenum in strongly acidic nitric acid medium.

Here, we present new experimental data on the speciation of molybdenum as a function of nitric acid concentration. Isotopically pure ^{98}Mo powder was dissolved in nitric acid and measured with the ALBATROS ESI-TOF[7]. Besides the presence of polymeric hexavalent Mo species the spectra show that pentavalent Mo species are present in solution in spite of the oxidizing condition in strong nitric acid.

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Interfacial dynamic in liquid/liquid extraction processes probed by non-linear optics

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A non linear optical technique namely second harmonic generation (SHG) is used to study the dynamics of an interfacial phenomena occurring during a liquid/liquid extraction. This process, involved in green chemistry for heavy ions recycling, consists in the selective transfer of ions from one liquid phase to another one leaving in contact. This transfer is obtain and more efficient using of liposoluble and ions complexant –molecules called extractants. The second harmonic generation (SHG), which consists in the conversion of two photons at the frequency ω in one photon at the doubled frequency 2ω, is a very sensitive surface technique because is forbidden in centrosymetric media [1]. The studied system is made of a water/dodecane interface, with extractants monoamide (DEHiBA) in the organic phase [2] and nitric ions in aqueous phase, in the frame of uranium ore extraction. We have shown for the first time that SHG measurements at equilibrium can be correlated with tensiometry measurements. Then, at out of equilibrium, kinetics with different regimes as well as a dynamic highlighted through correlation function [3] were characterized as a function of the extractant concentration [4]. Thanks to this technique, we show that extractant molecules could interact and form aggregate at the interface in a highly fluctuant way. This happens for an extractant concentration which is lower than those above which aggregates are detected (with SAXS) in the organic bulk phase. A deeper analysis of this interfacial process could permit to better understand the kinetics of ion transfer at a liquid/liquid interface and to be able to simulate it for industrial application [5]. This project will be extend to systems such as BTP-type complexant known to be characterized by low kinetic of ion transfer (SACSESS project).

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Influence of ionic strength on U(VI) sorption on montmorillonite at high salinities

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Clay and clay minerals are potentially suitable as host rock for nuclear waste disposals due to their high sorption capacities and low permeability. In Germany, there are two types of clay that in principle are eligible to be used for the construction of deep geological disposals: South German Opalinus clay with low ionic strength pore waters and north German clay deposits with high ionic strength pore waters, e. g. with sodium chloride concentrations of up to 4 mol/l in the depths relevant for nuclear waste disposal [1]. The present work focuses on U(VI) sorption onto the clay mineral montmorillonite under high ionic strength conditions, with the Konrad mine serving as reference site for experimental conditions. The experiments are conducted in sodium and calcium chloride as well as in a mixed electrolyte that resembles the groundwater at the Konrad site.

The classic ionic strength effect, where sorption decreases with increasing ionic strength, can only be observed in the acidic pH range where cation exchange is the predominant sorption mechanism for U(VI). However, natural groundwaters at the Konrad site have pH values from 5.75 to 6.85, where the ionic strength has an already diminished influence on sorption. The sorption maxima for U(VI) in the different salt systems lie slightly below the neutral point and well within the pH range of groundwaters of the reference site. For high ionic strengths like those in north German groundwaters, U(VI) retention becomes partly irreversible [2]. Furthermore, in the calcium chloride system, U(VI) retention increases strongly with ionic strength in the alkaline pH range. Both these effects are attributed to secondary phase formation, which is promoted by increasing ionic strength.

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Solubility properties of the Ln-rhabdophane compounds: $LnPO_4.nH_2O$ (Ln = La → Dy), precursor of the monazite phase

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The rhabdophane phases $LnPO_4.nH_2O$ (Ln = La-Dy), are used as low temperature precursor for the synthesis of the monazite, considered as a promising host matrix for the specific conditioning of minor actinides [1]. During lixiviation of monazites [2], the rhabdophane phases could also control the release of actinides in solution [3]. Therefore, it is necessary to obtain reliable solubility constants of the $LnPO_4.nH_2O$ (Ln = La-Dy) series through over-saturation experiments (precipitation of the phase of interest) and under-saturation experiments (leaching of the phase of interest). Speciation calculations were further made thanks to Phreeqc 2 software implemented with the thermodynamic data LLNL [4,5] and provided access to solubility products of rhabdophane phases in standard conditions (Equation 1).

$$LnPO_4.xH_2O \leftrightarrows Ln^{3+} + PO_4^{3-} + xH_2O \text{ and } K^{\circ}_{s,0} = (Ln^{3+})(PO_4^{3-}) \quad \text{Equation 1}$$

with (i), activity of the species i in solution.

The experiments performed at different temperatures allowed the determination of thermodynamic data (variation of free energy, enthalpy and entropy of the reaction) linked to the leaching and the formation of these phases. The values obtained by over and under-saturation experiments were found to be similar: $-26.0 < pK°_{s,0} < -24.4$. Moreover, samples from leaching tests were analyzed by PXRD, and only rhabdophane phase was observed, which confirm the reliability of our solubility values. This first multiparametric study on rhabdophane solubility represents the first step of the investigation of the monazite solubility, since rhabdophane phases are often observed as neoformed phases during the leaching of monazite phases.

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Experimental and computational simulation of radiation damages

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Crystalline ceramic matrices for the conditioning of minor actinides and Pu may suffer from self-irradiation damage due to α-decay that may result in a crystalline to amorphous transformation over time [1, 2], depending on the α-dose and the material's properties. For example zircon can be amorphized rather easily, while monazite has a quite high resistance to irradiation [3] and Zr-pyrochlore changes its crystal structure instead of getting amorphous [4]. Alpha self-irradiation may lead to changes in physical properties, cracking, and a reduced chemical durability of the waste form. Therefore, efforts are necessary to investigate the impacts of radiation damage on the durability of ceramic waste forms.
Various methods can be used to simulate damages emerging from irradiation processes, experimental as well as computational approaches. Experiments are complex as either the handling of short-lived actinides or the use of particle accelerators are required. The way of simulating radiation effects in the material closest to reality is the incorporation of short-lived radionuclides such as ^{238}Pu or ^{244}Cm. Moreover, different kinds of external irradiations can be performed to generate radiation damages. The most common approaches are the bombardment with α-particles or heavy ions and the irradiation with neutrons.
Furthermore, the effects of α-decay and of the recoiling nuclei can be simulated with computer programs like SRIM [5, 6]. This software package uses Monte-Carlo simulations to describe the range and transport of particles in materials. The simulation of displacement cascades allows the calculation of dose rates in dpa (displacements per atom) that can be used to compare and evaluate data of external and internal irradiation.
The presentation will give an overview of several experimental methods causing radiation damages and some possible analytical methods to detect them. In addition, the contribution of computational simulations using SRIM will be discussed.

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Optical floating zone method and accelerated crucible rotation technique – Two different approaches of growing single-crystals -

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Since single-crystals are applied in various fields, and every field has its own demands regarding size, shape, purity and quality of the crystals, different growth methods are used for getting the best possible crystals for their respective application. Therefore, two approaches of growing crystals are presented: the Optical Floating Zone Method (OFZM), and the Accelerated Crucible Rotation Technique (ACRT) for high temperature solution growth.

Zone melting is used in purification processes of metals, alloys and semiconductor compounds (Pamplin, 1975; Wilke, 1963), such as copper (Tolmie & Robins, 1956, 1957), aluminium antimonite (Schell, 1955) or germanium (Trousil, 1955). Originally designed in a horizontal installation (Pfann, 1952), the set-up was constantly modified. Today, crystals are usually grown vertically without a crucible. One of these methods is the OFZM, which was developed by Keck & Golay (1953, 1954), Emeis (1954) and Theuerer (1956, 1962).

In this approach, a polycrystalline “feed rod”, which is moved through the hot zone of the furnace, and a polycrystalline “seed rod” are vertically collinear. The melt is held between these rods because of its surface tension (Pamplin, 1975). The geometry of the configuration allows for obtaining single-crystals due to fundamental crystal growth mechanisms.

Hence, the advantage of OFZM is that chemically highly pure single-crystals are obtained.

The ACRT is an improvement of the high-temperature solution growth (flux) method (Scheel & Schulz-Dubois, 1971). Different materials are used as fluxes (e.g., molten salts, oxides; Elwell & Scheel, 1975). Potentially, single-crystals obtained by this method are more “perfect” than crystals grown from the melt, because the growth is closer to the equilibrium.

ACRT induces special homogenisation mechanisms in the melt by variation of rotation rates of the crucible (Scheel, 1972). By this, spontaneous and heterogeneous nucleation, lattice defects and inclusions can be avoided due to sophisticated control of the growth rate.

Hence, the advantage of crystals grown by ACRT is that they are nearly free from thermal strain and have a low defect density (several orders of magnitude lower than crystals grown, e.g., by OFZM).

Actinide chemistry under extreme conditions: the new high pressure / high temperature facility at Jülich research center

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The chemistry of Actinides is of special interest because the knowledge of their chemical behavior is of great importance for applications linked to nuclear energy production and nuclear repositories. In addition, these elements are very interesting as the objects for basic experimental and theoretical studies because they possess 5f-electrons.

Recently, most experimental studies on Actinide chemistry are done at ambient or mild hydrothermal pressures. The use of high pressure / high temperature equipment could expand the range of experimental spectrum and therefor the understanding of actinide chemistry enormously.

In November 2013 a new high pressure / high temperature facility was established at the Institute of Energy and Climate Research (IEK-6) of the Jülich research center. The new combined piston cylinder / multi anvil press (Voggenreiter LP 1000/540–50) is a tool for producing high hydrostatic pressures and simultaneous high temperatures on relatively large sample sizes (compared to diamond anvil cell). The high-pressure modules can be replaced within a few minutes on the press. Both technologies have different advantages that complement each other perfectly. The multi anvil module offers the ability to generate high pressures of up to 24 Giga Pascal (GPa) and a very precise control of the pressure and temperature conditions, while the piston cylinder module has a relatively simple sample structure and significantly increased sample volume and also a very precise control of the pressure and temperature conditions. In addition it has significantly shorter operating times between the experiments (30-60 minutes per cycle). For the multi anvil module 3 different setups were available:

- 18/11: p_{min}= 4 GPa, p_{max}= 10 GPa, sample volume up to 15 mg;
- 14/8: p_{min}= 8 GPa, p_{max}= 15 GPa, sample volume up to 10 mg;
- 10/4: p_{min}= 15 GPa, p_{max}= 24 GPa, sample volume up to 5 mg;

  T_{max} for all setups ~2300°C.

For the piston cylinder module 2 different setups were available:

- ¾ ´´: p_{min}= 0.3 GPa, p_{max}= 2.5 GPa, T_{max}: 1500°C, sample volume up to 800 mg;
- ½ ´´: p_{min}= 0.5 GPa, p_{max}= 4 GPa, T_{max}: 1800°C, sample volume up to 125 mg.

The different setups of the combined piston cylinder / multi anvil press have overlapping pressure ranges. This helps to prevent experimental sources of errors. The machine is in regular use since December 2013. Some results will be presented on the Poster by Na Yu, Vladislav V. Klepov and Evgeny V. Alekseev.

Single crystal x-ray diffraction and its application in actinide studies

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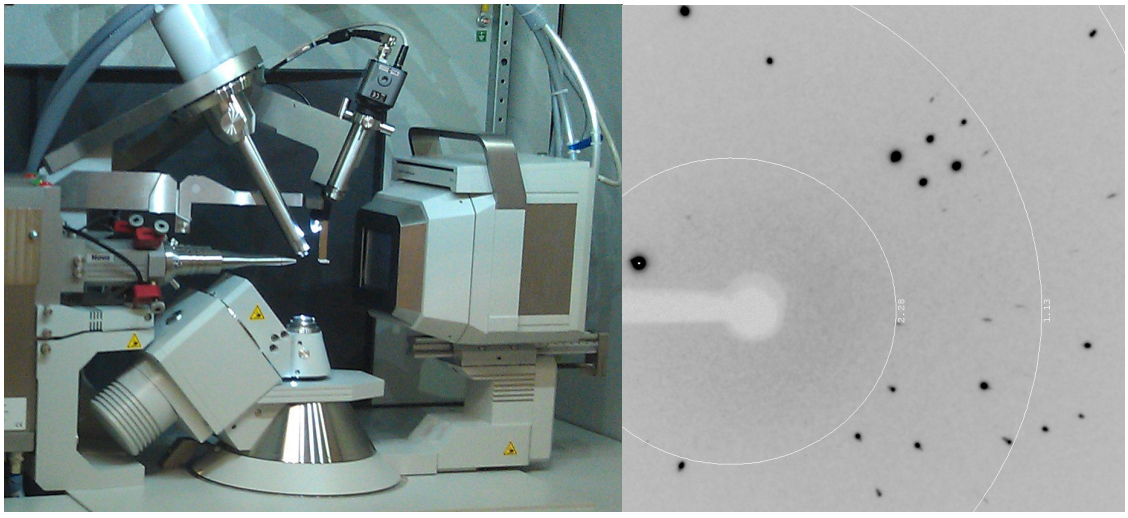
The single crystal X-ray diffraction (SG XRD) starts its history with the pioneer experiments of Max von Laue in 1912. This method first only allowed to determine crystal structures of the simple compounds (e.g. NaCl, NaBr, NaI) and then was significantly developed during the 20st century. Nowadays, SG XRD is employed to evaluate crystal structures of huge molecules, such as proteins. Among more than 1 million studied and deposited in international crystal structures databases, over 95% were studied by SG XRD.
In this contribution, some basic aspects, implementations and limitations of SG XRD were discussed. Furthermore, the X-ray basics were supported by an example of regular SG XRD experiment with a crystal obtained from a high temperature high pressure (HTHP) work. Besides, the structure of obtained crystal $Th(As^{III}_4As^{V}_4O_{18})$, which is the first example of a mixed valence As(III)/As(V) actinide compound, was discussed.



Nuclear waste management on supercomputers: Reliable modelling of f-elements-bearing ceramic materials

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With the increasing power of supercomputing resources and the functionality of scientific software it is now possible to simulate the properties of even chemically complex materials using ab initio, i.e. first principle methods of quantum chemistry. However, because of strong electronic correlations, f-elements-bearing materials, such as lanthanide- and actinide-bearing ceramics, are difficult to compute reliably by the standard ab initio methods such as density functional theory. We will discuss the origin of these difficulties on the example of monazite-type ceramics. We will show how various properties of these materials could still be reliably computed with carefully selected, affordable methods of computational quantum chemistry. Last but not least, we will show how reliable atomistic modelling approach can complement the experimental studies in order to obtain better understanding of the investigated materials.

Extraction of Ta and Nb with an alternative procedure using the pre-ouzo effect

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It has been discovered recently[1], that a mixture of water/ethanol/1-octanol creates nanoscopic aggregates, referred to as the pre-ouzo effect. These structures are located near the two-phase border and possess properties similar to those of a microemulsion. Besides, it is well known, that 1-octanol has an ability to selectively extract Tantalum and Niobium, depending on the pH of the aqueous phase[2].
In this work, we want to take advantage of the big effective surfaces offered by the pre-ouzo effect to emphasize Ta-extraction. This alternative extraction procedure is ecologically and economically beneficial, as no further extractant molecule besides 1-octanol is being used.
The influence of pH, ionic force and different hydrotropes on the ternary phase diagram has been investigated. Furthermore, the shift of the phase transition as a function of the temperature lied in the focus of investigation, to determine the optimal extraction area. More effective extractions were obtained at lower acidic concentrations compared to the classic liquid-liquid-extraction.

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X-ray absorption fine spectroscopy on the Rossendorf Beamline

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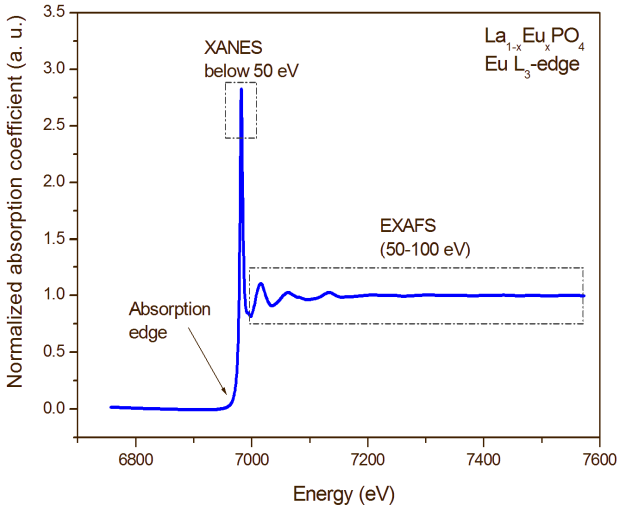
In the early 1970's, the fusion between the modern theory of XAFS (X-ray Absorption Fine Spectroscopy) and the development of dedicated Synchrotron sources [1], led to a breakthrough in the understanding of complex structures which conventional techniques such as XRD (X-ray Diffraction) could not solve. While XRD is well suited to determine the lattice structure of ordered matter, it could do nothing when such an order is not present; XAFS in contrast is ideally suited to investigate amorphous materials, highly disordered systems and liquids. XAFS derives electronic information by analyzing of how X-rays are absorbed by a specific type of atom at energies near and above its core-level binding energies. The XAFS measurement derive also local structural information from the oscillatory structure in the X-ray absorption coefficient just above the X-ray absorption edge Furthermore, the XAFS signal is the weighted statistical average of all atoms of one type of element in a sample, hence allows to identify the all chemical species of the probed element and their quantitative distribution (speciation) [2]. XAFS is applicable to a wide range of problems across all disciplines of the physical, chemical and biological sciences.

A typical XAFS spectrum is divided into two regimes: XANES (X-ray Absorption Near-Edge Spectroscopy) and EXAFS (Extended x-ray Absorption Fine Structure). XANES is strongly sensitive to formal oxidation state and coordination symmetry (e.g., tetrahedral, octahedral) of the absorbing atom; while EXAFS is used to analyze the neighbors of the excited atoms, i.e. coordination number, atomic distances and disorder. The aim of this work is to give a review of the general EXAFS theory and experimental aspects passing through the considerations that must be taken into account to run a successful XAFS experiment. Explicitly, we will discuss its application for the speciation of radionuclides at low concentrations and in complex matrices. Finally, examples and limitations of this technique at the Rossendorf Beamline will be shown.



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Comparison of mass-spectrometry, atomic emission spectrometry and gamma spectrometry for determination of rare earth elements

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For separation and pre-concentration of the rare earth elements (REE) it is important to control their concentrations in solutions on the each stage of extraction process. Since each sample contains about fourteen elements with different concentrations varying from 0.1 to 100 mg/L and similar chemical behavior, the quantitative determination of individual REEs becomes complicated.

In this work to determine the distribution ratios of REE between aqueous and organic phases three methods have been applied, i.e. atomic emission spectroscopy with inductively coupled plasma (ICP-AES); mass spectrometry with inductively coupled plasma (ICP-MS) and gamma spectrometry (GS). Here each of these methods is briefly discussed:

Method	ICP-MS	ICP-AES	GS
Element characteristics	Mass to charge ratio	Wavelength of EMR	Energy of γ-rays
Detection limit (g/L)	10^{-15} to 10^{-8}	10^{-8} to 10^{-5}	>50mBq
Destructive method	yes	yes	no
Time of measurement	5-10 min	1-5 min	1 min – 10 hours
Drawbacks	Influence of surrounding matrix	Influence of isobars and molecule ions	Using radiotracers, Constant geometry of sample

In ICP-MS and ICP-AES methods as ionizing agent inductively coupled plasma is used. For both methods the calibration standards are required. In the case of GS calibration standard is not necessary for calculation of relative values (ratio of REE in two phases). GS and AES are similar in source of analytical signal – in both methods electromagnetic radiation is detected. But in AES EMR is produced by electronic transitions and in GS by nuclear transitions so they account to dramatically different range of energy.

Result: Distribution coefficients calculated from data obtained by three techniques are presented in fig.1. Determination by gamma spectrometry was done for Ce-144, Eu-152 and Nd-147. Relative standard deviation for Kds calculated by ICP-MS and GS is about 10%. Data from ICP-MS and GS show close values. Larger difference between AES and other methods can be explained by complicated emission spectra of REEs (interference of emission and absorption lines) and by difference of detection limits.

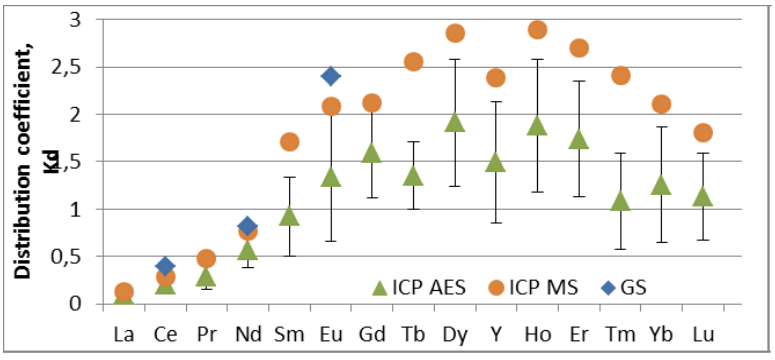

Fig. 1 Kd. for REEs calculated from different techniques

The monoclinic form of the rhabdophane compounds: $REEPO_4$. 0.625 H_2O

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Hydrated rhabdophane with a general formula $REEPO_4$. nH_2O (REE: La→Dy) has been always considered as crystallizing in an hexagonal structure. A recent re-examination of this system by the use of synchrotron powder data of the $SmPO_4.0.625H_2O$ compound led to a structure crystallizing in the monoclinic C2 space group with a = 28.0903(1) Å, b = 6.9466(1) Å, c= 12.0304(1) Å, β = 115.23(1)° and V = 2123.4 (1) $Å^3$ with 24 formula units per unit cell. The structure consists of infinite channels oriented along the [101] direction and formed by the connection of Sm-polyhedra and P-tetrahedra through the share of O-edges. The water molecules filling the space have been localized for the first time. The monoclinic form of the hydrated rhabdophane was confirmed complete of the series with REE: La→Dy. Moreover, the dehydration of $SmPO_4.0.625H_2O$ led to the stabilization of an anhydrous form $SmPO_4$ in the C2 space group with a = 12.14426 (1) Å, b = 7.01776(1) Å, c= 6.34755(1) Å, β = 90.02 (1)°, V = 540.97(1) $Å^3$ and Z =6.

Uptake of *f*-elements by iron chelators: what can we learn from thermodynamic and kinetic solution studies?

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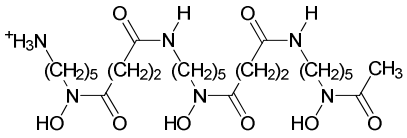
The management and remediation of uranium-contaminated fields and the disposal of nuclear wastes in deep geological repositories are societal issues of great concern. Predicting the behavior of actinides under environmental conditions is of paramount importance, but modeling their speciation in waters and soils requires an accurate knowledge of the thermodynamic and kinetic parameters related to their complex formation and dissociation equilibria. In particular, migration and bioavailability of actinides in the biosphere are highly dependent upon the presence of organic ligands.[1] Because such data are scarce and often unreliable in the case of the transuranium cations, considerable research efforts are still required.[2]

Our aim is to investigate the coordination chemistry in aqueous media of selected 4f and 5f elements with environmentally-relevant, widespread chelators, namely natural and abiotic hydroxamic acids. The former, also called siderophores, are excreted by most bacteria and some yeasts to supply them with iron(III). However, desferrioxamines, pyoverdines, and rhodotorulic acid have recently been shown to form stable complexes with various actinides and to efficiently mediate plutonium uptake by several bacterial strains.[3]



Desferrioxamine B (DFB)

The lecture will focus on desferrioxamine B, an ubiquitous open-chain trishydroxamic siderophore which is present in soils at micromolar concentration levels, as well as on some abiotic systems considered as model ligands. By combining classical potentiometric and UV-vis spectrophotometric titration techniques with capillary electrophoresis, EXAFS and RAMAN spectroscopies, the speciation of the different systems could be unraveled and structures for the various complexes prevailing in solution proposed. Finally, the proton-assisted dissociation mechanism of the uranyl chelate will be discussed.

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Preparation of microparticle reference materials for nuclear safeguards particle analysis

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In order to deter non-nuclear weapon states signatory to the Non-Proliferation Treaty from acquiring nuclear weapons, the International Atomic Energy Agency conducts inspections in facilities and sites situating nuclear-related activities. During these inspections, on-site measurements are performed and samples are taken. A relative new field in the nuclear safeguards analytics is the analysis of particles collected through swipe sampling during inspections. In dedicated laboratories the swipe samples are scanned for microparticles which are then analyzed by mass spectrometric methods, e.g. secondary ion mass spectrometry (SIMS) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). When particles containing uranium of plutonium are discovered, the elemental and isotopic compositions are determined with high precision. The presence and composition of detected microparticles can provide insight into activities in the facility, specifically the production or handling of undeclared materials.

As the results obtained in particle analysis are relevant to conclude the absence of undeclared activities, there is great need for proper quality control and quality assurance to ensure the quality of the analysis results. Therefore, calibration standards and reference materials are required. At present, no relevant reference material consisting of uranium microparticles is available. Current work at the Forschungszentrum Jülich focusses on the preparation of monodisperse microparticles consisting of uranium oxide with specific elemental content per particle and specific isotope ratios. This is achieved by generating an uranyl nitrate aerosol using a vibrating orifice aerosol generator (VOAG). The prepared aerosols are thermally denitrated and collected. Monodisperse uranium microspheres have been obtained and the prepared particles are currently characterized.

Future work focuses on the embedment of the produced microparticles into a solid matrix for simplified handling, storage, transport and measurement. Suitable matrix materials have to be selected and possible synthesis methods are to be considered. Furthermore, the stability of the microparticles and the matrix material are to be investigated and possible particle-matrix interactions are to be identified.

Microorganisms and their impact on radionuclide speciation

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Microorganisms are ubiquitous in the environment. Hence, for the long-term safety assessment of a nuclear waste repository it is necessary to know which microorganisms are present in the potential host rocks (e.g., clay) and how these microorganisms can influence the performance of a repository. The Opalinus clay layer of the Mont Terri Underground Rock Laboratory (Switzerland) is one potential host rock for nuclear waste disposal [1]. It is well known that indigenous bacteria in such underground environments can affect the speciation and the mobility of actinides [2-5].

From our point of view, the understanding of the speciation and the structure of the actinide (An)/lanthanide (Ln) complexes formed in presence of indigenous bacteria over a wide range of geochemical parameters (e.g., pH, metal concentration) becomes indispensable for predicting the safety of a planned nuclear waste repository.

Our research is focused on broaden the knowledge concerning the bacterial diversity in potential host rocks for nuclear waste storage (e.g., Mont Terri Opalinus Clay) by applying direct molecular culture-independent retrievals and cultivation experiments. After cultivation and characterization of dominant bacterial populations we investigate their influence on the geo-chemical behaviour of selected An/Ln (uranium, plutonium, and curium/europium). The indirect (e.g., actinide mobilization by microbially produced bioligands) and direct (e.g., biosorption, bioaccumulation, biotransformation) influence of microorganisms on the speciation/migration processes of An/Ln will be highlighted during the lecture by using selected examples. This helps to understand the manifold interaction processes in such biological systems on a molecular level.

Acknowledgements. The authors thank the BMWi for financial support (contract no.: 02E9985, 02E10618 and 02E10971) and the BGR for providing the clay samples.

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Immobilization of long-lived radionuclides by incorporation into repository relevant ceramics (Conditioning)

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The disposal of high level radioactive waste is one of the most pressing and demanding challenges, since more than 1800 metric tonnes of Pu, and substantial quantities of the ‘‘minor’’ actinides, such as Np, Am and Cm, have been generated in nuclear reactors during the past 60 years worldwide[1]. With respect to long-term safety aspects of geological disposal, the “minor” actinides and long-lived fission and activation products such as ^{36}Cl, ^{135}Cs, ^{79}Se and ^{129}I may be of particular concern due to their long half-lifes, their high radiotoxicity and mobility in a repository system, respectively. Ceramic waste forms for the immobilization of these radionuclides have been investigated extensively in the last decades since they seem to exhibit certain advantages compared to other waste forms (e.g. borosilicate glasses and spent fuel) such as high waste loadings and chemical durability[2]. Currently, most on-going nuclear waste management strategies do not include ceramic waste forms. However, it is still important to study this option, e.g. with respect to specific waste streams and certain constraints regarding deep geological disposal.

Within this communication the role of ceramic waste forms within the framework of innovative waste management strategies, such as Partitioning&Transmutation&Conditioning (P&T&C) concept will be discussed. A general overview of promising single-phase and multi-phase ceramic waste forms will be presented incl. their merits compared to other waste forms. A particular attention will be paid to the current understanding regarding the materials science of ceramic materials for the immobilization of high-level nuclear waste and their long-term behavior under conditions relevant to geological disposal.

Various aspects will be addressed focusing on single phase waste forms, such as monazite and zirconates with pyrochlore structure:

1.) synthesis methods suitable for the safe handling of radionuclides such as sol-gel route, hydrothermal synthesis and co-precipitation, 2.) structural and microstructural characterization using state-of-the-art spectroscopic / diffraction (TRLFS, Raman, XRD) and microscopic techniques (SEM), 3.) thermodynamic stability and reactivity under conditions relevant for nuclear disposal, in particular with respect to leaching / corrosion in aqueous environments as well as 4.) studies on radiation damages. Finally, a refined understanding of these aspects on a molecular level will help to improve long-term safety assessments of deep geological disposal concepts using these waste forms.

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Solubility thermodynamics of tetrapropyl- and tetrabutylammonium pertechnetates

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The production of metallic technetium is an important stage of the manufacture of targets for the transmutation of technetium. An appropriate compound is to form a precipitate that can be easily converted to the metal. For this purpose such compounds as TcO_2, Tc_2S_7, NH_4TcO_4, Ph_4AsTcO_4 can be used. In this work the salts formed by Tc tetraoxo anions with the tetrapropyl- and tetrabutylammonium cations ($(C_3H_7)_4N^+$ (Pr_4N^+) and $(C_4H_9)_4N^+$ (Bu_4N^+)) are presented. Pr_4NTcO_4 and Bu_4NTcO_4 generate easily combustible wastes. The insufficiency of thermodynamic data for these compounds due to not considering the activities ($\gamma_\pm$) was noted in [1]. In this study, the solubility and some thermodynamic characteristics of tetrapropyl- and tetrabutylammonium pertechnetates have been determined with special respect to this point.

The solubility product of $(C_nH_{2n+1})_4NTcO_4$ has been calculated using the following equation:

$$SP = \gamma_\pm^2[(C_nH_{2n+1})_4N^+][TcO_4^-],$$

where $\gamma_\pm$ - an activity coefficient; n = 3, 4.

The solubility product of Pr_4NTcO_4 is $(6.2 \pm 0.2) \times 10^{-5}$ mol^2/L^2. The Gibbs energy of dissolution of $[(C_3H_7)_4N]TcO_4$ in dilute aqueous solutions is 24.0 ± 0.5 kJ/mol (T = 298 K).

The solubility product of Bu_4NTcO_4 is $(1.6 \pm 0.2) \times 10^{-5}$ mol^2/L^2. The Gibbs energy of dissolution of $[(C_4H_9)_4N]TcO_4$ in dilute aqueous solutions is 27.4 ± 0.5 kJ/mol. The temperature dependence of solubility has been found. The enthalpy and entropy of dissolution are 14.9 ± 0.4 kJ/mol and –42.0 ± 0.7 kJ/mol×K correspondingly. The solubility of $(C_nH_{2n+1})_4NTcO_4$ (n = 3, 4) increases with the solution acidity and decreases with the augmentation of $[(C_nH_{2n+1})_4]OH$ concentration.

For precipitation of technetium from spend nuclear fuel solutions to transfer technetium into metal or carbide for the following transmutation, tetrapropyl- and tetrabutylammonium pertechnetates are recommended to be used, the tetrapentylammonium analogue is under study.

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Non-nuclear applications – Separation of rare earth elements

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Rare earth elements (REE=Ln+Sc+Y) have similar physical and chemical properties and tend to occur in the same ore deposits. Despite being classified as rare earths, they are relatively abundant in the Earth's crust, with cerium being about as abundant as copper [1]. Nearly 200 REE minerals are known, but approximately 95% of all the world rare earth resources occur in just three minerals: bastnasite $REE(CO_3)F$, and phosphates ($REE(PO_4)$) with monazite and xenotime structure [2].

The largest REE deposits are found in China, Australia, and the United States. Although, China possesses approximately only 23% of the world's rare earth deposits, in recent years China controls more than 97% of the global supply of rare earth metals. During the last decades the demand for rare earths increases as a result of rising technology applications (124,000 tons in 2012 and predicted between 200,000-240,000 tons in 2020). As a result of the increased demand and tightening restrictions on exports of REE from China, it is necessary to restart and build new plants and to optimize the REE separation [3].

The separation is the last and the most value creating step of REE refining and beneficiation. Due to the similar physical and chemical properties of REE, separation of two directly neighboring elements shows the largest scientific and technical challenge.

Here, we describe different separation processes of REE [1, 4, 5]. We focus on the solvent extraction, which is the most advantageous technique for REE separation. An overview of two industrially used extraction agents and their separation properties [6] will show how many stage numbers are needed to achieve a good separation between neighboring elements.

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Multi-functional molecules used in complex formulations of extracting fluids

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The studies of phenomena which govern the ion selectivity (thermodynamic and kinetic) as well as the understanding of the migration mechanism at interfaces (kinetic, diffusion) and the improvement of the chemical separation processes (liquid/liquid, solid/liquid, membranes…) are of a great interest in the field of recycling and more generally for the sustainable development. Whatever the technology, the selectivity towards a target results from the properties of the dispersant medium (aqueous, organic solvent, ionic liquid), the physical and chemical stimuli (temperature, acidity), also from a perfect adequacy between the coordination mode, the spatial arrangement and the nature of the chelating sites of the ligand (hard/soft, denticity, pre-organization), sometimes to the detriment of the affinity.
With the concomitant development of supramolecular chemistry and coordination chemistry, spectacular progress in the field of ion separation led to the development of chemical libraries of ligands with various size, nature and structure such as cryptands, coronands, podands, heterocycles and cyclophanes. The design of the structures, their rigidity or flexibility, their stereochemistry as well as the nature, the number and the arrangement of the chelating sites are established according to their more or less pronounced affinity and selectivity with the considered metal target.
In this lecture, we focus on the different strategies used in the design, synthesis and study of ligands increasingly efficient and selective.

Speciation of actinides using synchrotron radiation techniques

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Speciation is an important analytical discipline since the environmental behavior of heavy metals, including actinides, depends on their chemical form, i.e., their oxidation state and molecular structure. The application of synchrotron radiation (SR) techniques to actinide environmental sciences has grown considerably during the last two decades[1,2]. The unique information that can be obtained from SR studies has contributed significantly to a fundamental understanding of, for example, sorption phenomena, complex and colloid formations, as well as redox transformations of actinides in abiotic and biotic systems.
The presentation will give a brief introduction to the principles of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies and summarize what type of information can be obtained. The advent of high-energy resolution XANES spectroscopy of actinide materials will be discussed as well[3].
Since many natural systems possess a high degree of spatial heterogeneity, investigations with micrometer SR beams have become increasingly important. Micro X-ray fluorescence (μ-XRF) mappings provide the spatial distribution of elements on a sample surface. The speciation of actinides in areas of high concentration can be investigated by μ-XANES and μ-EXAFS. Micro X-ray diffraction (μ-XRD) allows the identification of associated crystalline phases. Recent examples will illustrate the potential of these spatially resolved SR methods and their contribution to a molecular-level understanding of the environmental behavior of actinide[4].

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Synergistic mechanism in liquid-liquid extraction: role of water - effect on interfacial film curvature

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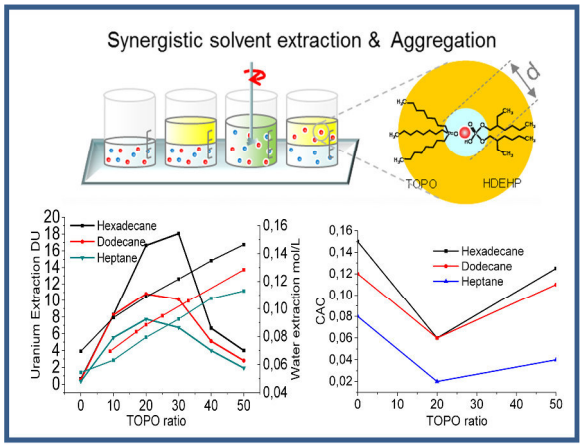

Fig. 1 Extraction of Uranium and aggregation of HDEHP/TOPO.

In solvent extraction, a concentrated solution of mixed salts is contacted with an organic phase that can be considered as a reverse microemulsion, in which some salts are selectively extracted. When mixed extractants are used in the formulation of the microemulsion, “synergism” of yet unknown origin emerges: at a specific ratio of extractant, an increase of distribution coefficients is observed.

The origin of synergism is in some cases not clear because in chemical engineering modelling implies usually chelation and not micellisation. The synergistic system HDEHP/TOPO was chosen as model system. It was studied in different diluents to observe their influence on extraction and aggregation because they are not expected to affect the chelation properties. Experiments have shown that for all the solvents the optimized uranium extraction remains at a synergistic TOPO ratio of 20%. Meanwhile, when increasing the carbon chain length of diluent, uranium extraction appeared to become more efficient. Finally, the synergistic extraction as well as the solvent effect were found to be related to the swelling of the aggregates with water extraction. To rely all these phenomena, it was therefore proposed to explain the underlying mechanisms by estimating the bending energy of the system.

Microscale study of Np speciation during diffusion in natural clay

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Argillaceous rocks are considered as a potential host rock formation and principal component of barrier and backfill materials of high-level nuclear waste repositories. Due to the long half-life (2.14×10^6 a) and high radiotoxicity of ^{237}Np, neptunium, together with other actinides, plays an important role in the long-term safety assessment of future repositories.
The interaction of Np with clay during diffusion was investigated on a molecular scale using a combination of spatially-resolved synchrotron based techniques that are available at the micro XAS beamline of the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland), i.e., micro X-ray fluorescence (µ-XRF) and micro X-ray absorption near-edge structure (µ-XANES) spectroscopy. The distribution and speciation of Np in Opalinus Clay (OPA, Mont Terri, Switzerland) was investigated after diffusion of Np(V) into natural clay cores. Using the advantage of a micro-focus synchrotron beam of approximately 2 µm diameter, it was possible to determine the Np speciation along its diffusion path, despite the diluted concentrations. µ-XRF maps showed the distribution of Np and other elements contained in OPA (i.e., Ca, Fe). In several Np hot spots, Np(IV) was identified as the dominating species in OPA after the diffusion process by Np L_{III}-edge µ-XANES spectroscopy. Highly soluble Np(V) was reduced progressively along its diffusion path to the less mobile Np(IV) species. The reducing properties of OPA are a positive result with respect to the safety assessment of radioactive waste disposal in argillaceous rocks. As demonstrated convincingly be the present study, the X-ray microprobe is a powerful analytical tool which can provide detailed chemical images of the reactive transport of actinides in heterogeneous natural systems.
This work was supported by BMWi (contract No. 02E10981) and TALISMAN.

Colloid/Nanoparticle formation and radionuclide mobility determining processes investigated by laser- and synchrotron based techniques

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Transport of pollutants can occur in the aqueous phase or for strongly sorbing pollutants associated on mobile solid phases spanning the range from a couple of nanometers up to approx. ~1µm; usually called colloids or nanoparticles [1,2]. A challenge with respect to understand and predict the radionuclide mobility is the radionuclide speciation, the mineral surface interaction and the mobility of nanoparticles. Especially for colloid/nanoparticle associated contaminant transport the metal sorption reversibility is a key element for long-term mobility prediction. The spatial resolution needed is clearly demanding for nanoscopic techniques benefiting from the new technical developments in the laser and synchrotron community [3]. Furthermore, high energy resolution is needed to resolve different chemical species or the oxidation state of redox sensitive elements. In addition, chemical sensitivity and post processing methods extracting chemical information from a complex matrix are required.

The presentation will give examples of homogeneous and heterogeneous nucleation of nano-particles [4], the speciation of radionuclides through incorporation in these newly formed phases [5], the changes of surface roughness and charge heterogeneity and its impact on nanoparticle mobility [6]. Furthermore, flow path heterogeneity is driving the mobility/ retention of colloids/ nanoparticles, which can be resolved by tomographic (CT) methods [7]. Reactive transport models usually use simplified geometrical assumptions which are essential to properly predict pore clogging. Examples of nanoparticle transport up-scaling from laboratory scale (µm-dm) to field scale experiments will be discussed and current challenges and potential new directions will be highlighted in the presentation.

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Uranium(VI) retention in clay and crystalline rock: How and why does it differ

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The long-term disposal of high-level nuclear waste in deep geological formations is discussed worldwide as a main strategy for nuclear waste management. This approach requires the use of a multiple barrier system consisting of engineered, geo-engineered, and geological barriers to prevent any release of radionuclides into the geo- and biosphere. Sorption of radionuclides on the host rock of a repository is one important process for retarding their migration. Potential host rocks for nuclear waste repositories that are investigated internationally are salt domes, clay rock, and crystalline rock.

In the present work, the retention behavior of clay and crystalline rock towards U(VI) is compared. For this, sorption of U(VI) onto Opalinus Clay from the Mont Terri rock laboratory (Switzerland) was studied in the presence of Opalinus Clay pore water (pH = 7.6; I = 0.36 M) [1]. This is compared to U(VI) sorption onto anoxic diorite from Äspö Hard Rock Laboratory (Sweden) that was studied in the presence of Äspö groundwater (pH = 7.8; I = 0.18 M) [2]. The impact of various parameters, such as solid-to-liquid ratio, initial U(VI) concentration, temperature and atmosphere, on U(VI) sorption was studied.

Distribution coefficients, K_d values, determined for the U(VI) sorption onto Opalinus Clay and diorite at 25 °C, amount to 22.2 ± 0.4 L/kg [1] and 3.8 ± 0.6 L/kg [2], respectively. Thus, U(VI) sorption onto Opalinus Clay is stronger than onto diorite, which can be attributed to its larger surface area. TRLFS and ATR FT-IR spectroscopic measurements showed that the U(VI) speciation in Opalinus Clay pore water as well as in diorite groundwater is predominated by the weakly sorbing $Ca_2UO_2(CO_3)_3(aq)$ complex. Reduction processes of U play only a subordinate role. The U(VI) sorption increases with increasing temperature.

U(VI) diffusion experiments with intact Opalinus Clay bore cores [3] also showed that Opalinus Clay has a good retardation potential for U(VI) since the molecular diffusion process through Opalinus Clay retards the migration of $Ca_2UO_2(CO_3)_3(aq)$.

Generally, it can be concluded that U(VI) retention by clay rock is stronger than that by crystalline rock. This supports decisions to use clay rock not only as host rock but also as backfill material. In case of crystalline rock the natural retention capacity for U is insufficient and has to be strengthened by additional geo-technical and technical barriers that preserve their enclosing capabilities over very long time scales.

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[3] Joseph, C. et al. (2013) Geochim. Cosmochim. Acta 109, 74-89.

Radiation stability of partitioning relevant ligands for minor actinide separation

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In several European projects, various strategies for partitioning of minor actinides from PUREX raffinates were investigated with the aim of reducing the radiotoxicity and heat production of high level waste. Most of the heat generation results from radioactive decay of the fission products within the first hundreds of years. For longer timescales, plutonium and the minor actinides dominate heat generation.
For minor actinide partitioning diglycolamides (DGAs, Figure 1) and bistrianzinepyridines (BTPs, Figure 2) are applied for liquid-liquid extraction processes. DGAs contain oxygen as hard donor atoms which are able to separate f-elements from the fission products. In contrary BTPs contain the soft electron donor nitrogen which allows them to separate actinides from lanthanides.
For the development of processes on an industrial scale resulting in much longer contact times of the ligands with high active waste, a detailed knowledge of the hydrolytic and radiolytic stability of these extracting agents is mandatory.

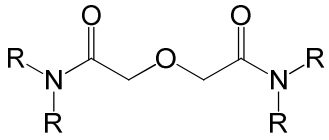

Figure1: Diglycolamide, general structure

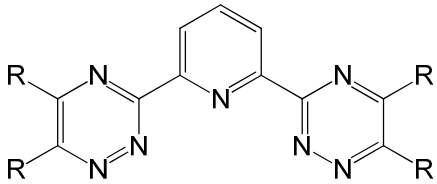

Figure2: Bistriazinepyridine, general structure

In order to investigate the mechanisms of radiolysis and the impact to liquid-liquid extraction, a ^{60}Co (~10 kGy/h) source was used to irradiate organic solutions of ligands under different conditions. The degradation products were determined by UV/VIS, IR and Raman spectroscopy as well as HPLC-HRMS analysis.
First mass spectrometric results of BTPs in octanol show both, an addition of one or two octanol groups to the ligand molecule, as well as degradation of the molecules. In addition to structural analysis, liquid-liquid extraction experiments with ^{241}Am and ^{152}Eu trace solutions were performed. It turns out that the distribution ratios D_{Am} and D_{Eu} decrease with increasing doses. Further studies are planned to investigate the influence of different dose rates and radiation types.

Ultra-trace analysis of Pu, Np, and Tc using resonance ionization mass spectrometry (RIMS)

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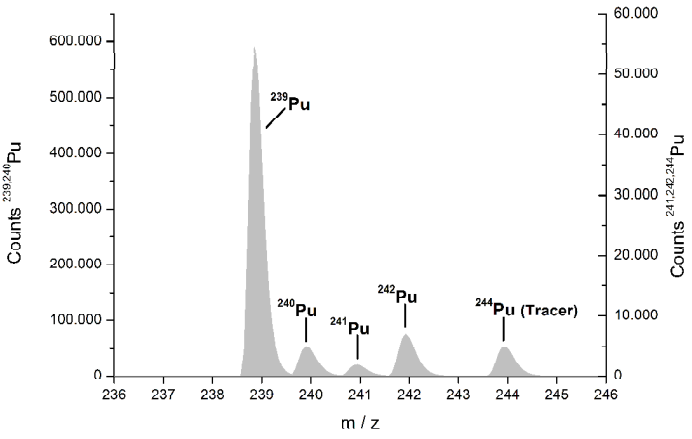
Resonance ionization mass spectrometry (RIMS) is a powerful tool for ultra-trace analysis and isotope ratio measurements of long-lived radionuclides and is applied to samples with concentrations below the detection limits of conventional radiometric methods or when isobaric interferences are encountered, which are common in mass spectrometry. RIMS provides very high isobaric suppression and mass spectra with very low background resulting in detection limits down to 10^6 atoms per sample. [1]

In RIMS the atoms in an atomic beam are ionized by two- or three-step resonant laser excitation. The laser ions are mass separated in a time-of-flight spectrometer and counted by a multi-channel plate detector. Due to the uniqueness of the optical transitions, high elemental selectivity and a nearly complete suppression of atomic and molecular isobaric interferences are achieved. Before the RIMS measurement, the element under investigation has to be chemically separated from the matrix and electrodeposited on a filament. While the measurement of environmental samples for Pu is well established and routinely applied, similar procedures have been developed recently for ^{237}Np and ^{99}Tc in our group. For the quantification of the isotope of interest, a known amount of a tracer isotope of the same element, e.g., ^{244}Pu, is added prior to the chemical treatment of the sample. During the measurement, sample and tracer isotopes are selectively ionized by alternately tuning the lasers to their respective transition wavelengths. The presentation will show the experimental setup and the excitation schemes for the analysis of $^{239\text{-}242}$Pu, ^{237}Np and ^{99}Tc using RIMS. As an example, the figure below shows a mass spectrum of Pu isotopes in an environmental sample collected near Sellafield, UK, in which the Pu isotopes with mass numbers 239, 240, 241, and 242 were quantified using RIMS.



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Sorption of Pu(III) onto Opalinus Clay – Influence of pH and ionic strength

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Plutonium is a major contributor to the radiotixicity of spent nuclear fuel after storage times of more than thousand years due to ^{239}Pu, which is an alpha particle emitter with a half-life of 2.411×10^4 years. Knowledge of the migration behaviour of plutonium in the host rock of the repository is important for its long-term safety assessment. Argillaceous rocks are considered by several European countries, including Germany, as a potential host rock for the geological disposal of high-level nuclear waste. Due to reducing conditions present in argillaceous rocks and the high salinities of pore waters in such clay formations in Northern Germany, we investigated the sorption behaviour of ^{239}Pu(III) as a function of pH and ionic strength in NaCl solutions.

Opalinus Clay (OPA) from Mont Terri, Switzerland, was used as a reference for natural clay. The batch experiments were performed with 4×10^{-7} M Pu(III) in the pH range 1-10 in 0.1 M NaCl in a glove box under argon atmosphere ($O_2 \leq 10$ ppm). During the experiments pH and E_h were monitored regularly. The sorption of the redox stable analogue ^{241}Am(III) was measured for comparison, except that the experiments were performed under ambient air conditions.

The sorption curves of Pu(III) and Am(III) in 0.1 M NaCl showed completely identical behaviour. The sorption increased with pH from ~10% at pH 2 to 100% at pH ≥ 6. The pH edge (50% sorption) occurred at pH ~4.5. It should be noted that according to the measured E_h values in the suspensions Pu(IV) might have been present in the batch samples at pH ≥ 6. Therefore, the oxidation states of the two actinides taken up by the clay might be different at pH ≥ 6, despite the same sorption values.

The influence of 0.01, 0.1, 1, 2, and 3 M NaCl on the sorption of 4×10^{-7} M Pu(III) on OPA was investigated both at pH 8 and near the pH edge, i.e., at pH 4. As expected, ionic strength had no influence at pH 8 due to the complete uptake of Pu. At pH 4 the highest uptake of ~64% Pu(III) was observed in 0.01 M NaCl. The Pu uptake decreased with increasing ionic strength and equalled ~20% for 1-3 M NaCl. This ionic strength dependence points to cation exchange as the dominating sorption mechanism for Pu(III) on OPA at pH 4.

In conclusion, although both Pu and Am are taken up completely by Opalinus Clay at near neutral pH and no effect of ionic strength could be observed, the speciation of Pu and the reversibility of its uptake should be investigated in the future since different dissolved species, i.e., Pu(IV) and Am(III), were deduced at pH ≥ 6.

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Production of simulated fuel particles and analytical characterization methods

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Partitioning and transmutation (P&T) is a promising method to safely handle minor actinides which origin from energy production by nuclear fission. In this concept, actinide co-conversion processes play an important role to close the fuel cycle. During the heterogeneous recycling of minor actinides, oxidic materials containing uranium as main matrix are used as innovative nuclear fuel.

The focus of research is on the production of simulated fuel particles. A dustless preparation method is the sol-gel route via internal gelation (IG) [1], where an aqueous colloidal solution is transformed into a solid particle. Another promising concept is the weak-acid resin process (WAR) [2]. During this process, weak-acid cation exchange resins are loaded with ions.

In this work, both methods were used to fabricate microspheres consisting of a homogeneous mixture of U and Nd. Neodymium acts as a surrogate for trivalent actinides, such as americium. Mass and size characteristics of the particles prepared by IG have been studied. Finally, the particles were sintered in a reducing atmosphere and the products have been investigated by SEM/EDX and XRD.

In order to investigate simulated fuel particles prepared by the WAR, the ion exchange resins Amberlite IRC-86 and Lewatit TP-207 were loaded with UO_2^{2+} and Nd^{3+}. Various parameters have been investigated to maximize the adsorption. A thermal treatment has been carried out and the products were analyzed by SEM/EDX and XRD.

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Determination of La and Eu by ICP-AES and gamma-spectrometry

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The challenging problem in production of rare-earth elements is their separation and extraction in individual forms from their mixture, since they exhibit similar chemical properties. Despite many existing methods, the most convenient for industrial applications is the liquid-liquid extraction. Disubstituted organic phosphoric (for example, commonly used di-(2-ethylhexyl) phosphoric acid, D2EHPA) and phosphonic acids represent one of the most widely used classes of extractants. In the present work we study the extraction effectiveness and selectivity of new analogs of D2EHPA. For this purpose the determination of REEs' concentrations in aqueous and organic phases should be performed with high accuracy.

To verify quantitative determination of REE in the present paper ICP-AES and gamma spectrometry using radioactive tracers were applied. In our experiments we used model solutions with Eu^{3+} and La^{3+} in 10^{-5} - 10^{-3} M concentration range.

Gamma spectrometry could be used to determine the trace contents of the elements in the liquid or solid samples without pretreatment and sample preparation. Addition of radioactive tracer to stable cation provide us the tool to follow chemical distribution between organic and aqueous phases. The detection limit is the concentration of radiotracer that could be down to 10^{-10} M for Eu-152. Thus, the element can be detected at any stage of the multi-stage separation process.

ICP-AES - a way to determine the elemental composition of the material on the optical emission line spectra of atoms and ions of the excited states. It is the most common, express and sensitive method to identify and quantify the elements in liquid and solid substances. It is widely used in various fields of science and technology for the control of industrial production, search and processing of minerals, biological, medical and environmental studies, etc. ICP-AES allows to determine the content of metals at concentrations of 10^{-8}-10^{-5} g/L, but in the analysis of a mixture of substances with low concentrations interferences with other elements can lead to high errors. In the model experiments, where only one REE is present, no difficulties in determination of La or Eu concentrations by ICP AES was established, that was independently confirmed by gamma-spectrometry.

Application of gamma-spectrometry and LSC for determination of rare earth elements.

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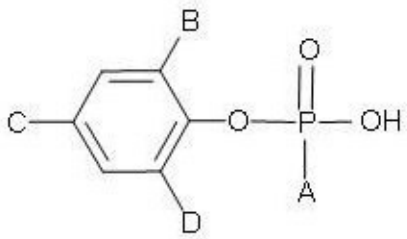
Rare earth elements (REE) are widely used in the production of various advanced functional materials because of their unique properties. In this connection, the separation of individual REE metals from their mixtures is an important technological task. The main industrial method of separation of REE is liquid-liquid extraction with organophosphorus compounds, such as TBP, D2EHPA, PC-88A. However complete separation of a mixture of REE using mentioned extractants requires a large number of extraction steps or sustained maintaining definite conditions, e.g. pH value. In this regard, the search for new selective and effective extractants remains relevant today. One of the most promising classes of phosphorus compounds are organic acids having a low viscosity in concentrated solutions that are synthesized from readily available starting materials. The aim of this work is to determine the extraction properties of new aryl-containing organophosphorus acids :



Where:

1) A = -O-t-Bu, B, D = -t-Bu, C = -Me
2) A = -O-$(CH_2)_2$-O-CH_3, B, D = -t-Bu, C = -Me,
3) A, B = -t-Bu, C = -Me, D = -O-$(CH_2)_2$-ph
4) A =-O-2-, 6-diisopropylphenyl, B, D = -i-Pr, C = -H,
5) A =ph, B, C = -H, D = -i-Pr,
6) A = -O-CH_2-$CH(C_2H_5)$-$(CH_2)_3$-CH_3, B, D = -Me, C = -H,
7) A = -O-CH_2-$CH(C_2H_5)$-$(CH_2)_3$-CH_3, B, C, D = -H,

The experiment represented a single extraction individual lanthanide nitrate (10^{-5}M Ce^{3+} or Y^{3+}) in a solution of the test ligand in toluene from the aqueous phase: pH 1-5, 1M $NaNO_3$. To follow content of the metal cations in the aqueous and organic phases we used ^{144}Ce and ^{90}Y radiotracers. In our model experiments both stable cation and its tracer were used in the same form as nitrate solutions that is very important for this method. The distribution of Y^{3+} could be easily determined by liquid scintillation counting of ^{90}Y in organic and aqueous phases. For registration of ^{144}Ce by gamma-spectrometry organic phase needs to be stripped prior to measurements since toluene can provide increased efficiency in gamma counting. Stripping was performed by 3M HNO_3 and lead to non-detectable residue of cation in organic phase. Based on the results of tests organic phosphorus acids for further studies were selected, that demonstrated the possibility of effective separation of REE, i.e. 1, 5, 7 ligands. Calculated distribution coefficients as a function of pH and ligand concentration allowed us to suggest following reaction of the extraction:

$$Me^{3+} + 2\overline{HL} + NO_3^- = \overline{Me(HL)_2NO_3} + 2H^+$$

Preparation of Palladium nanoparticles by photolysis and evolution of physicochemical properties

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At the last time a physicochemical property of nanoparticles and dependence on each other are investigated very active. However, there are very few works, investigating the evolution of these properties in a time.

In this work we investigated the evolution of physicochemical property of palladium nanoparticles in time. A ξ-potential, hydrodynamic diameter and catalytic activity were studied.

Very stable during long time nanoparticles were prepared by means of photochemical method. The photochemical method is irradiation of solution containing palladium complexes and stabilizing agent by pulsed xenon lamp. When irradiated of solution, highly active radicals and molecules were produced. They reduced palladium complexes to Pd^0. The formed sol of palladium is monodispersed and has average diameter of 2.5 nm.

Catalytic activity of palladium nanoparticles was studied in the reaction of single-electron reduction of methylviologen dichloride in the alkaline aqueous medium (pH = 11.0) by hydrogen. Standard potential of pair is $E_0(MV^{2+}/MV^{\cdot+}) = -0.450$ V. The potential of hydrogen pair is substantially more negative, namely $E_0(H^+/H_2) = -0.652$ V, because the hydrogen ion concentration is low. By these conditions the next reaction becomes possible:

$$2MV^{2+} + H_2 + 2OH^- \rightarrow 2MV^{\cdot+} + 2H_2O$$

The formed radical cation $MV^{\cdot+}$ is blue, therefore its concentration was measured by spectrophotometry ($\varepsilon_{600}(MV^{\cdot+}) = 1.1\times10^4$ l·mol^{-1}·cm^{-1}) [2]. This reaction is a reaction of the first order with respect to hydrogen and is described by the next kinetic equation:

$$[MV^{\cdot+}] = [MV^{\cdot+}]_\infty \cdot e^{-k\tau}$$

When studying properties of palladium nanoparticles it has been shown that the hydrodynamic diameter of the sol increases uniformly in time to 15 nm and then slowly decreases to 14 nm. The dependence between the rate constant of catalytic reaction and the zeta-potential on one part and time on the other part has a linear form with a kink. Kink of lines occur on the third day after preparation of palladium nanoparticles.

Thus, the study of the evolution of physical and chemical properties of nanoparticles allows to control and to drive their catalytic properties.

This work was supported by the Russian Found of Basic Research (Project Grant Nos. 12-03-00449-a).

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Plane wave parallel plate ultrasound spectroscopy on ceramic pellets

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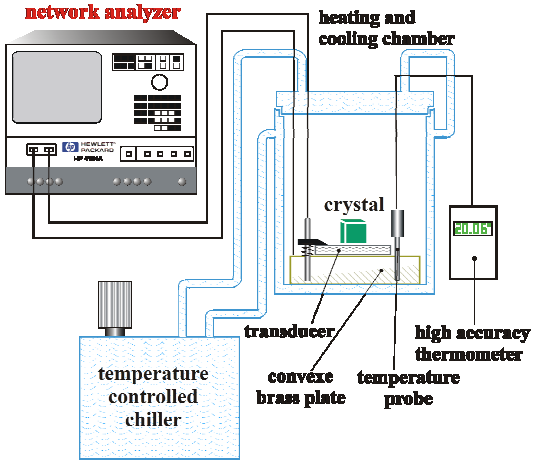
Plane wave / parallel plate ultrasound spectroscopy is a non-destructive technique for deriving elastic stiffness coefficients. In case of an isotropic material the sample have to be polished plan-parallel in an arbitrary orientation. The resonance frequencies can be measured through the extinction of mechanical oscillations in the sample, using an ultrasound transducer which is driven by an impedance analyzer. For the coupling of the ultrasound wave paraffin oil or resin (Fig.1) should be applied. Resonance frequencies can be detected by measuring the phase angle between the current and the voltage (Arbeck et al. 2010).

The distances between these resonant frequencies peaks are equidistant thus it is possible to calculate the sound velocities by: v=2D (Δf) where (Δf) is the difference between two neighboring resonate peaks and D is the thickness of the sample. In equation 2 the relation between the ultrasonic velocities and the elastic coefficients is given, where c_{ij} are the elastic coefficients and ρ is the density (Yadawa et al. 2009) $c_{ij}=\rho v^2$ (2).

The used ceramics are homogenous and isotropic. Therefore just the velocities of longitudinal and shear waves (Fig.1) are needed to calculate mechanical properties like the Bulk modulus or the Young's modulus.



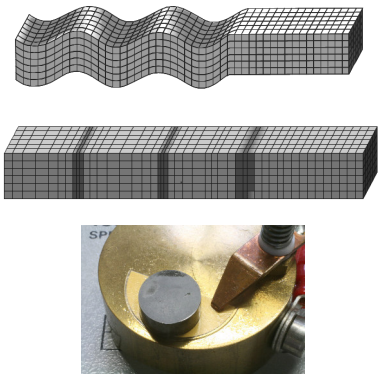


Figure 1: Left: Experimental setup. Right: Propagation directions of longitudinal - (top) and shear (middle) waves. Picture of a coupled sample (below).

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Immobilization of long-lived iodine after incorporation into apatite and layered double hydroxide matrices

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Iodine-129 being long-lived volatile fission product, among with cesium-135 and technitium-99, represents a challenge for the design of repository-suited matrices [1]. The present study investigates a possibility of iodine incorporation in the forms of iodide and iodate into apatite and layered double hydroxide (LDH) matrices. The matrice should meet certain requirements, *i.e.* being cheap, safe, easy to synthesize, stable and environmental friendly. Optimization of coprecipitation method for synthesis of iodine containing apatite and LDH has been done. It was shown that iodide practically does not incorporate in case of apatite and that incorporation is lower in comparison to iodate in case of LDH. However, apatite incorporates *ca.* 5 - 7 % of iodate. Obtained matrices are structurally characterized by XRD and EXAFS methods. EXAFS showed that the iodate-apatite obtained via coprecipitation has a single prominent I – O scattering path at a distance of 1.8 Å. Thermogravimetric analysis of the iodate-apatite showed the release of iodine at t > 550ºC, whereas in case of LDH the iodine is released at 180ºC. The leaching experiments with LDH showed that more than 50 % of iodine is released after one day in brine solution. Therefore, apatite seems to be suitable matrice for iodine immobilization for a long-term, whereas LDH can be used for a short-term only.

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Metal(III) Complexes of *meso*-phosphorylated porphyrins: synthesis and self-assembling

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Recently, the efficient synthesis and self-assembling of *β*- and *meso*-dialkoxyphosphoryl-substituted porphyrins according to Hirao reaction were reported [1-5]. The self-assembling of their zinc(II) and copper(II) complexes led to the original supramolecular architectures of 1D, 2D and dimeric structures indicating that this series of functionalized porphyrins are promising molecular building blocks for material science.

The introduction of trivalent metals to phosphorylporphyrins should open new possibilities of processes of supramolecular association through P=O…M axial interactions using coordination contacts along with electrostatic interactions. Here we report the synthesis and self-assembling ability of various complexes of *meso*-mono-(diethoxyphosphoryl)porphyrins with trivalent metals (Mn(III), Ga(III), In(III)) as well as their monoesters and phosphonic acid derivatives. Examples of molecular InPor(Cl) (fig. 1) and supramolecular $[Ga(Por)(py)]_2$ (fig.2) structures of obtained compounds are presented.

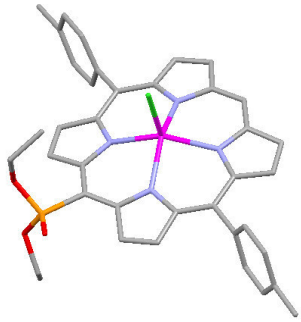

Fig.1.

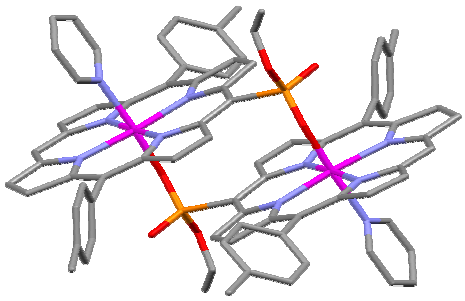

Fig.2.

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Combined chemical and structural investigations of $Ba_xRa_{1-x}SO_4$ on the atomic level by TEM and APT

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Experimental studies related to long-term safety assessments for the deep geological disposal of spent nuclear fuel suggest that Ra and the formation of the $Ba_xRa_{1-x}SO_4$ solid solution will be relevant in this context. Doerner and Hoskins derived thermodynamic properties for the formation of the $Ba_xRa_{1-x}SO_4$ solid solution, e.g. the partition coefficient, from kinetically influenced co-precipitation experiments [1]. Their model is based on assumptions about the uptake and distribution of Ra in the $Ba_xRa_{1-x}SO_4$ solid.
We [2] followed a close-to-equilibrium approach and carried out ToF-SIMS analysis of the solid indicating a homogeneous uptake of Ra into the solid in amounts as predicted by thermodynamic calculations [3]. However, for a detailed investigation of the recrystallization process, nano-analytical methods need to be established in order to investigate the homogeneity of the Ra distribution.
Transmission electron microscopy (TEM) provides detailed structural information and is a well-established technique for many different materials. There has been a major progress in the resolution of TEM due to aberration correction [4]. For the detailed chemical analysis of a sample, atom probe tomography is a powerful tool with resolution up to the atomic level. Since the development of the laser-assisted Atom Probe Tomography (APT), the analysis of electrically non-conductive samples is possible [5]. The combination of these two methods makes the achievement of both structural and chemical information at the atomic level possible. By using a special sample holder, even the analysis of the same sample with both methods is possible.
Here, we present a method development for the combined characterization of $BaSO_4$ (barite) by atom probe tomography (APT) and transmission electron microscopy (TEM). This method will be later applied to the characterization of $Ba_xRa_{1-x}SO_4$. Preparation is done by focused ion beam (FIB) from particles with a size of 10 - 40 µm. Electrical non-conductivity and poor thermal conductivity of barite leaves the APT-analysis of this mineral challenging.

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Development & demonstration of actinide separation processes in Europe

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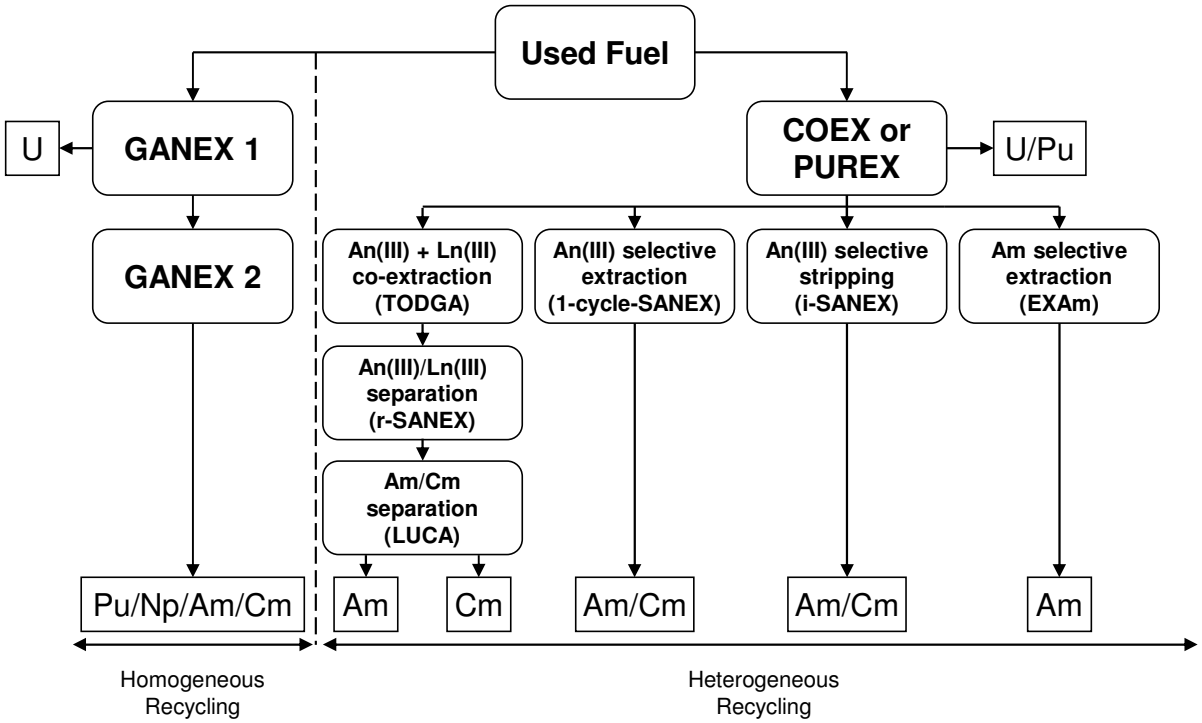
This paper gives an overview of the recent developments in Europe concerning innovative partitioning processes for the treatment of used nuclear fuel. The different fuel cycle strategies homogeneous vs. heterogeneous recycling will addressed, together with the corresponding separation processes. The process development and demonstration will be presented and a comparison between the different processes will be given.



Redox speciation of neptunium using capillary electrophoresis coupled to ICP-MS

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^{237}Np ($t_{1/2} = 2.14 \times 10^6$ a), besides other actinides, is part of the high-level radioactive waste in spent nuclear fuels. The nuclear waste will be stored in a deep geological repository with argillaceous and crystalline rocks or salt as potential host rocks. Under natural conditions, Np^{IV} and Np^{V} are the dominating oxidation states in aquifers. The design of the repository has to ensure that the radioactive waste is isolated from the environment for periods of up to one million years. Therefore, for the safety assessment of a future geological repository it is very important to gain a deep understanding of the geochemical behavior of Np. For this reason it is essential to have a reliable and efficient analytical method for determining the exact speciation of Np at environmentally-relevant concentrations as in the case of a possible leakage from the repository.

For analyzing the Np oxidation states +IV and +V, the separation capability of capillary electrophoresis (CE) was coupled with the high sensitivity of ICP-MS. With this setup we achieved separation and quantification of different Np species within 20 minutes and limits of detections of approximately 1×10^{-9} mol/L[1].

To test the capability of CE-ICP-MS for determining redox kinetics of Np, the temperature dependence of the reaction of Np^{V} with hydroxylamine hydrochloride in hydrochloric acid solution was investigated. Hydroxylamine hydrochloride is a common reducing agent for the chemical reduction of Np^{V} to Np^{IV} and the kinetics has already been determined by UV-vis spectroscopy at millimolar concentrations[2]. Compared to the literature, the advantage of CE-ICP-MS is the fact that the required Np concentrations are about five orders of magnitude lower than in UV-vis spectroscopy.

The poster will present the CE-ICP-MS method and its application to the redox speciation of Np. We determined the rate constants of the pseudo first order reduction of Np^{V} by hydroxylamine hydrochloride in the temperature range from 40-80 °C. With these rate constants, the Arrhenius parameters of the reaction were calculated.

This work was supported by BMWi (contract No. 02E10981).

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Knudsen Effusion Mass Spectrometry

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The *Knudsen Effusion Mass Spectrometry (KEMS*) is an established vapour-pressure measuring device developed in the early 1900's by Martin Knudsen. The KEMS has attractive features, as high sensitivity and resolution under high vacuum conditions, and can be used for qualitative as well as for quantitative analysis [1].

The KEMS set-up, as it is used at ITU, is built into a 5 cm thick lead shielded glove box, making it suitable to study radioactive materials, like actinide compounds and irradiated fuel. The experiments done are twofold, not only is the KEMS used to perform partial pressure measurements on nuclear materials, but it is also used to study fission product release as part of post irradiation experiments. The measurements are for example used to predict element behavior during nuclear accidents.

The parameters measured in the KEMS are the temperature and intensities of the ion currents originating from the ionization of the gaseous species. From this it is possible to (1) identify all gaseous species forming the equilibrium vapour over the condensed phase in the Knudsen cell, (2) calculate equilibrium partial pressures, (3) compute thermodynamic properties as the enthalpy of formation and activity coefficients and (4) follow fission product release paths [1].

Fig. 1 shows a typical result of a KEMS experiment. It shows a release of Xe fission product together with He from irradiated Superfact fuel. Releases of Xe are observed at 750 K, 1600 K and 2250 K. The three releases are explained by different release mechanism. The first release at 750 K is due to the gas release along the open grain boundaries, the second release is explained by diffusion of micro bubbles through the grains and the final release is due to the matrix evaporation which allows the release of the trapped gas within the fuel structure. The latter release mechanism is well complemented by superimposing the UO_2 signal which becomes significant at the same temperature as the final xenon release [2].

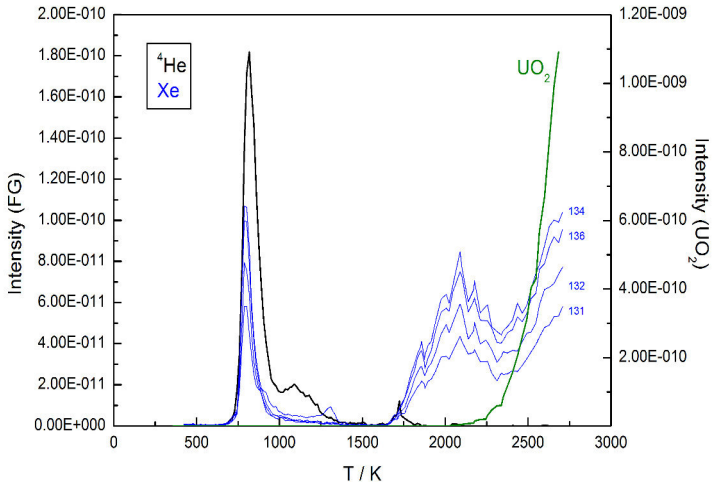

Figure 1: Fission product release of Xe and He from irradiated fuel measured by KEMS.

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